PB85-197093

Industrial Boiler SO2 Technology Update Report

Radian Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jul 84

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/3-85-009	2.	3. RECIPIENT'S ACCESSION NO. PB85 197093/AS
4. TITLE AND SUBTITLE Industrial Boiler SO_2 Technology Update Report		5. REPORT DATE July 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Ed Aul, Suzanne Margerum, Robert Berry, et al.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 3200 E. Chapel Hill Road/Nelson Highway Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-3816
12. SPONSORING AGENCY NAME AND ADDRESS Office of Air Quality Planning and Standards U. S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

Project Officer - Dale Pahl, OAQPS/ESED/MD-13

16. ABSTRACT

This document is a resource document for the development of Federal standards of performance for control of sulfur dioxide (SO_2) emissions for new industrial boilers. Various precombustion, combustion modification, and post combustion control technologies are identified with respect to each technology's applicability to industrial boilers, development status, and factors affecting performance. Emissions data for each technology are also presented. Post-combustion technologies examined include wet flue gas desulfurization (FGD) systems (sodium, dual alkali, lime, limestone) and dry processes (spray drying FGD, dry alkali injection, electron-beam irradiation). Combustion modification approaches examined include fluidized bed combustion, limestone injection multistage burners, and coal/limestone pellets. Precombustion approaches include physical coal cleaning, coal gasification, coal-liquid mixtures, and coal liquefaction.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
SO_2 Emissions Coal Air Pollution Industrial Boilers Pollution Control Technology Fuel Standards Coal Cleaning Flue Gas Desulfurization	Coal Air Pollution Control	

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 172
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

PB85-197093

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-85-009
July 1984

Air

EPA

Industrial Boiler SO_2 Technology Update Report

NSPS

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-450/3-85-009

Industrial Boiler SO2 Technology Update Report

Prepared by:
Radian Corporation
Under Contract No. 68-02-3816

Prepared for:
U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Emission Standards and Engineering Division
Research Triangle Park, NC 27711

July 1984

i.a

DISCLAIMER

This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication as received from the Radian Corporation. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. Copies of this report are available from the National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

TABLE OF CONTENTS

Page

CONTENTS i
LIST OF TABLES iv
LIST OF FIGURES vi

Chapter 1 - INTRODUCTION 1-1

Chapter 2 - POST COMBUSTION CONTROL APPROACHES 2-1

2.1 WET SCRUBBING PROCESSES 2-1

- 2.1.1 Sodium 2-1
    - 2.1.1.1 Process description 2-2
    - 2.1.1.2 Factors affecting performance 2-5
    - 2.1.1.3 Applicability to industrial boiler 2-12
    - 2.1.1.4 Development Status 2-29
    - 2.1.1.5 Reliability 2-29
    - 2.1.1.6 Emissions data 2-32
- 2.1.2 Dual Alkali 2-36
    - 2.1.2.1 Process description 2-38
    - 2.1.2.2 Factors affecting performance 2-39
    - 2.1.2.3 Applicability to industrial boilers 2-41
    - 2.1.2.4 Development status 2-43
    - 2.1.2.5 Reliability 2-44
    - 2.1.2.6 Emissions data 2-46
- 2.1.3 Limestone Wet Scrubbing 2-48
    - 2.1.3.1 Process description 2-50
    - 2.1.3.2 Factors affecting performance 2-50
    - 2.1.3.3 Applicability to industrial boilers 2-55
    - 2.1.3.4 Development status 2-57
    - 2.1.3.5 Reliability 2-61
    - 2.1.3.6 Emissions data 2-62
- 2.1.4 Lime Wet Scrubbing 2-62
    - 2.1.4.1 Process description 2-63
    - 2.1.4.2 Factors affecting performance 2-63
    - 2.1.4.3 Applicability to industrial boilers 2-65
    - 2.1.4.4 Development status 2-65
    - 2.1.4.5 Reliability 2-67
    - 2.1.4.6 Emissions data 2-69

TABLE OF CONTENTS (Continued)

2.2 DRY PROCESSES........ 2-70
  2.2.1 Spray Drying........ 2-70
    2.2.1.1 Process description........ 2-70
    2.2.1.2 Factors affecting performance........ 2-73
    2.2.1.3 Applicability to industrial boilers........ 2-75
    2.2.1.4 Development status........ 2-76
    2.2.1.5 Reliability........ 2-78
    2.2.1.6 Emissions data........ 2-79
  2.2.2 Dry Alkali Injection........ 2-81
    2.2.2.1 Process description........ 2-81
    2.2.2.2 Factors affecting performance........ 2-83
    2.2.2.3 Applicability to industrial boilers........ 2-84
    2.2.2.4 Development status........ 2-84
    2.2.2.5 Reliability........ 2-85
  2.2.3 Electron-Beam Irradiation........ 2-85
    2.2.3.1 Process description........ 2-85
    2.2.3.2 Status of development........ 2-87

2.3 REFERENCES........ 2-89

Chapter 3 - COMBUSTION MODIFICATION CONTROL APPROACHES........ 3-1

3.1 FLUIDIZED BED COMBUSTION........ 3-1

  3.1.1 Process description........ 3-2
  3.1.2 Factors affecting performance........ 3-6
  3.1.3 Applicability to industrial boilers........ 3-9
  3.1.4 Development status........ 3-12
  3.1.5 Emission test data........ 3-13

3.2 LIMB........ 3-16

  3.2.1 Process description........ 3-16
  3.2.2 Factors affecting performance........ 3-19
  3.2.3 Applicability to industrial boilers........ 3-19
  3.2.4 Development status........ 3-21
  3.2.5 Emissions data........ 3-22

3.3 COAL/LIMESTONE PELLETS........ 3-23

TABLE OF CONTENTS (Continued)

3.4 REFERENCES.. 3-24

Chapter 4 - PRECOMBUSTION CONTROL APPROACHES........................ 4-1

4.1 PHYSICAL COAL CLEANING... 4-1

4.1.1 Process description.. 4-1
4.1.2 Factors affecting performance................................ 4-2
4.1.3 Applicability to industrial boilers.......................... 4-3
4.1.4 Development status... 4-3
4.1.5 Performance.. 4-6

4.2 COAL GASIFICATION... 4-6

4.2.1 Process description.. 4-7
4.2.2 Factors affecting performance................................ 4-7
4.2.3 Applicability to industrial boilers.......................... 4-9
4.2.4 Development status... 4-10
4.2.5 Reliability.. 4-10
4.2.6 Performance.. 4-10

4.3 COAL-LIQUID MIXTURES.. 4-14

4.3.1 Process description.. 4-15
4.3.2 Factors affecting performance................................ 4-16
4.3.3 Applicability to industrial boilers.......................... 4-16
4.3.4 Development status... 4-17
4.3.5 Reliability.. 4-20
4.3.6 Emissions data... 4-20

4.4 COAL LIQUEFACTION... 4-21

4.4.1 Process description.. 4-21
4.4.2 Factors affecting performance................................ 4-25
4.4.3 Applicability to industrial boilers.......................... 4-27
4.4.4 Development status... 4-29
4.4.5 Reliability.. 4-31
4.4.6 Emissions data... 4-31

4.5 REFERENCES.. 4-37

LIST OF TABLES

Table Page

2.1-1 PREDOMINANT SODIUM SCRUBBING ABSORBER TYPES WITH THEIR THEIR TYPICAL SO_2 REMOVAL EFFICIENCIES AND OPERATING PARAMETERS........ 2-10

2.1-2 TABLE OF SODIUM SCRUBBING SYSTEMS........ 2-13

2.1-3 POPULATION OF SODIUM SCRUBBERS BY APPLICATION........ 2-22

2.1-4 TOTAL SO_2 TREATED BY APPLICATION FOR CURRENT SODIUM SCRUBBER SAMPLE........ 2-23

2.1-5 POPULATION OF SCRUBBERS ON UNITS FIRING OIL, COAL AND OTHER FUELS........ 2-24

2.1-6 POPULATION OF WASTE DISPOSAL METHODS OF SODIUM SCRUBBERS.... 2-25

2.1-7 RECENT RELIABILITY DATA FOR SODIUM SCRUBBERS........ 2-31

2.1-8 EMISSIONS DATA USING EPA TESTING METHODS........ 2-33

2.1-8a AVERAGE RESULTS FROM SODIUM SCRUBBING SYSTEMS........ 2-34

2.1-8b SO_2 REMOVAL EFFICIENCIES BY ABSORBER TYPE........ 2-35

2.1-9 APPLICABILITY OF DUAL ALKALI SYSTEMS INSTALLED ON INDUSTRIAL BOILERS........ 2-42

2.1-10 RELIABILITIES FOR DUAL ALKALI SYSTEMS........ 2-45

2.1-11 EMISSIONS DATA FOR DUAL ALKALI SYSTEMS USING EPA TESTING METHODS........ 2-47

2.1-12 SUMMARY OF LIMESTONE SYSTEMS OPERATING ON U. S. INDUSTRIAL BOILERS AS OF OCTOBER 1983........ 2-56

2.1-13 SUMMARY OF WET LIME FGD SYSTEMS INSTALLED ON U. S. INDUSTRIAL BOILERS AS OF OCTOBER 1983........ 2-66

2.1-14 THIOSORBIC LIME APPLICATIONS TO UTILITY BOILER FGD SYSTEMS........ 2-68

2.2-1 SUMMARY OF INDUSTRIAL BOILER SPRAY DRYING SYSTEMS........ 2-77

2.2-2 SUMMARY OF EMISSION DATA FOR FOUR INDUSTRIAL LIME SPRAY DRYING FGD SYSTEMS.................................. 2-80

3.1-1 PARTIAL SUMMARY OF COAL-FIRED INDUSTRIAL AFBC BOILERS IN THE U. S.................................. 3-11

3.1-2 SUMMARY OF SO_2 EMISSIONS DATA FOR VARIOUS AFBC CONFIGURATIONS.................................. 3-14

4.1-1 PREPARATION AND THERMAL DRYING OF BITUMINOUS COAL AND LIGNITE BY STATE - 1978 (THOUSAND) SHORT TONS............. 4-5

4.2-1 CURRENT APPLICATIONS OF LOW AND MEDIUM BTU GASIFICATION TECHNOLOGY.................................. 4-11

4.3-1 TEST EXPERIENCE WITH COM-FUELED PACKAGE WATERTUBE BOILERS.................................. 4-18

4.3-2 INSTALLED AND ANNOUNCED DOMESTIC COM PLANTS.................. 4-19

4.4-1 PROPERTIES OF SRC-II FUEL OILS AND COMPARABLE PETROLEUM PRODUCTS.................................. 4-30

4.4-2 EMISSION RESULTS FOR SRC TEST BURN AT PLANT MITCHELL.................................. 4-33

4.4-3 EMISSION RESULTS FOR DOE/PETC TESTS ON SRC.................. 4-36

LIST OF FIGURES

Figure Page

2.1-1 Process Flow Diagram for a Sodium Scrubbing System Using Soda Ash Slurry Storage.......... 2-3

2.1-2 Equilibrium partial pressure of SO_2 Over Aqueous Sodium Sulfite Solutions.......... 2-6

2.1-3 Limestone Process Flow Diagram.......... 2-51

2.2-1 Typical Spray/Dryer Particulate Collection Flow Diagram.......... 2-71

2.2-2 Dry Alkali Injection Flow Diagram.......... 2-82

2.2-3 E-beam/Ammonia Process Flow Diagram.......... 2-86

3.1-1 Schematics of Traditional Dense-Bed FBC Power-Generation Systems.......... 3-3

3.1-2 Schematics of Two-Stage and Circulating-bed AFBC Power-Generation Systems.......... 3-7

3.2-1 Multistage Combustion in a Distributed Mixing Burner (Top Half of Burner Only Depicted).......... 3-18

3.2.2 Fuel Rich Fireball Burner Design for Tangentially-Fired Boiler.......... 3-20

4.1-1 Kitt Mine Coal Preparation Plant - Hourly Incremental Data for Sulfur Dioxide Emission Parameter.......... 4-4

4.2-1 Low/Medium-Btu Gasification Process Options for Supplying an Industrial Boiler Fuel Gas.......... 4-8

4.4-1 Flow Diagram for SRC-I Demonstration Plant.......... 4-23

4.4-2 Flow Diagram for SRC-II Demonstration Plant.......... 4-26

1.0 INTRODUCTION

This document was prepared to provide the public and industry with additional background information on the industrial boiler source category in support of potential new source performance standards for sulfur dioxide (SO_2) emissions. The document is to be used as a supplement to the Background Information Document for Industrial Boilers prepared for the U. S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards by Radian Corporation in March 1982 and the series of Individual Technology Assessment Reports (ITARs) for industrial boiler applications prepared under the direction of EPA's Industrial Environmental Research Laboratory at Research Triangle Park, N.C. The overall objective of this report is to update the information and data contained in the above-referenced reports as it relates to SO_2 emission control technologies.

To minimize duplication of material, this document assumes that the reader is familiar with the earlier reports and makes liberal reference to those reports. In the case of some SO_2 control technologies, the principles of operation and factors affecting performance have changed to such a great extent that a substantial re-write of the technology description was in order. Where this is not the case, only supplemental information is presented.

The SO_2 control technologies selected for examination and updating are those which are either in current use by industrial boiler operators or under active investigation in research and development programs. The technologies are generally categorized as post combustion control approaches (Section 2.0), combustion modification control approaches (Section 3.0), and fuel pretreatment control approaches (Section 4.0). Each technology is discussed and evaluated from the standpoint of process principles, factors affecting performance, applicability to industrial boilers, development status, operability and reliability, emissions data, and process economics.

The process economics sections of this report contain information describing the impacts of process design and operating parameters on system costs. Direct comparisons of capital and annual costs for the technologies judged to be most applicable to industrial boilers for SO_2 emissions control are contained in the SO_2 Model Boiler Cost Report.

2.0 POST COMBUSTION CONTROL APPROACHES

Post combustion techniques for controlling SO_2 emissions from industrial boilers are discussed in this section. These techniques remove SO_2 from flue gases produced from fuel combustion. Post combustion techniques have been divided into wet and dry processes according to the final form of the recovered SO_2 product.

2.1 WET SCRUBBING PROCESSES

Wet flue gas desulfurization (FGD) processes use an alkaline solution or slurry to absorb SO_2 from boiler flue gas. The absorbed SO_2 exits the system either as a liquid waste stream or as a semi-solid waste sludge. The wet FGD processes discussed here are:

- Sodium
- Dual alkali
- Limestone
- Lime.

Each of these technologies is currently being used commercially to remove SO_2 from industrial boiler flue gases.

2.1.1 Sodium

Sodium scrubbing comprises approximately 98 percent of all industrial wet FGD installations and is treating roughly 80 percent of all the SO_2 treated by wet FGD scrubbers. If oil field generators are excluded from the industrial boiler population, then sodium scrubbers represent about 80 percent of the total industrial boiler wet FGD system population. The predominance of sodium scrubbers is primarily because of their ease of operation and their reliability, which is reported to be about 98 percent on average (see Section 2.1.1.5).

SO_2 removal efficiencies for sodium scrubbers have been consistently high. For tests conducted on 45 scrubbers using EPA testing methods, the average SO_2 removal efficiency was 96.2 percent with a standard deviation of 2.9 percent.

Sodium scrubbing is also the most economical of the wet FGD systems for most industrial boiler applications. For high sulfur coals, the total annualized costs (TAC) for sodium scrubbing systems become greater than TAC's for dual alkali systems in the 150 - 250 x 10^6 Btu/hr range. For low sulfur coals, this range is much beyond 400 x 10^6 Btu/hr, so that for all practical purposes sodium scrubbing is less expensive than dual alkali scrubbing for low sulfur industrial boiler applications. The predominant factors affecting total annualized costs are reagent and liquid treatment costs, which together comprise 65-85 percent of the total operating costs. Sodium scrubbing capital costs including wastewater treatment represent between 35 and 50 percent of dual alkali capital costs.

The March 1982 Background Information Document (BID) for Industrial Boilers assumed that sodium scrubbing use would be significantly limited by wastewater regulations. However, in many areas of the country, the wastewater stream is already being permitted by the local water authorities. Because of the assumption that the water regulations would be strict, it was predicted that treatment and disposal of the wastewater would be prohibitively expensive. It was therefore assumed that this technology would be applied only to those few plants that had either an inexpensive reagent source or a readily available disposal mechanism, or both. However, only about 20 percent of the plants currently using sodium scrubbers can be grouped into this category, indicating that wastewater treatment and disposal is not prohibitively expensive. For a further discussion of the wastewater issue, the reader is referred to Section 2.1.1.3.

2.1.1.1 Process Description. The following discussion includes additions and updates to the March 1982 BID and repeats only that information which is considered essential for the the discussions in the other sodium scrubbing sub-sections. A simplified sodium scrubbing process flow diagram is presented in Figure 2.1-1 to replace the one presented in the BID. Sulfur-dioxide is absorbed from boiler flue gases into an aqueous

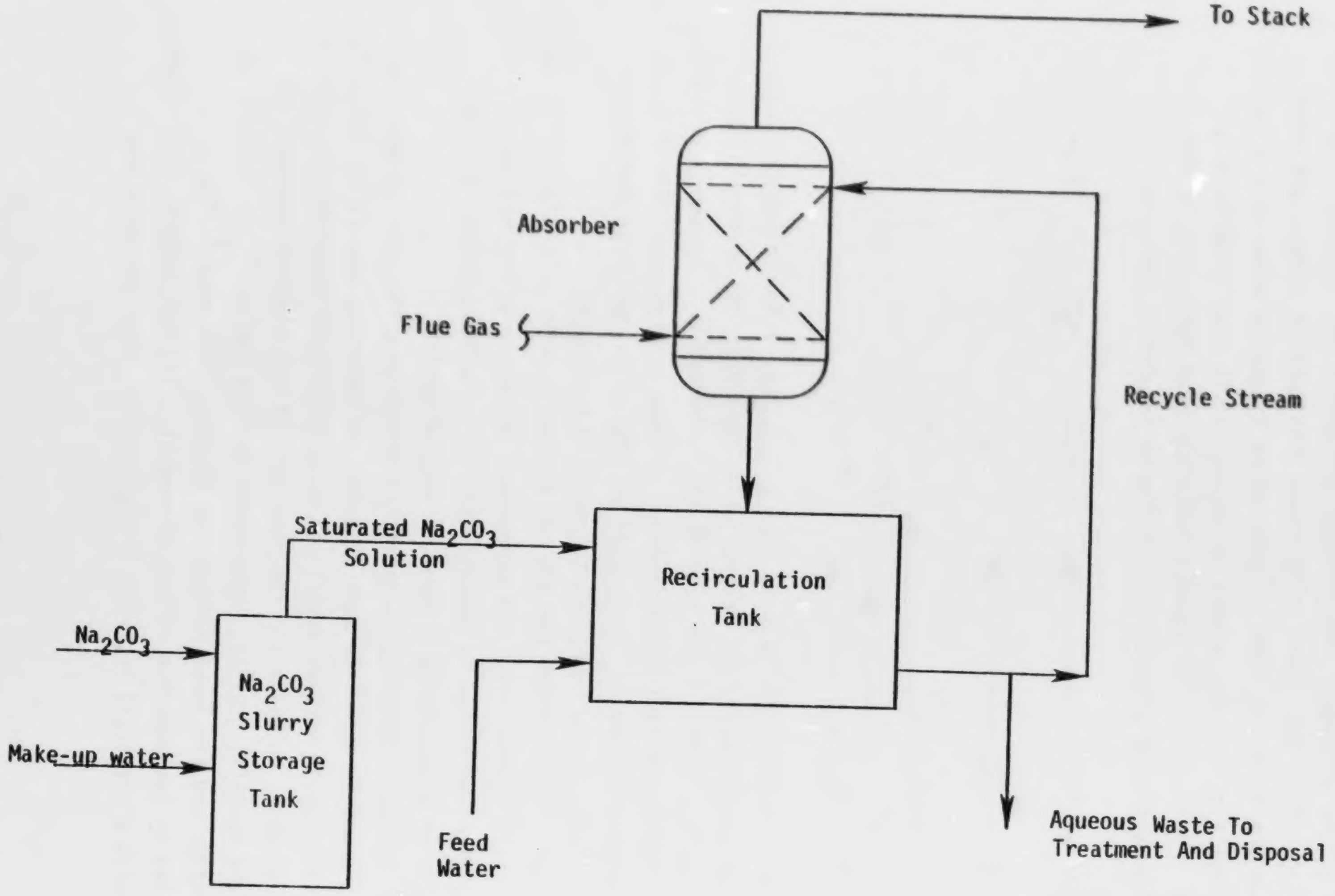

To Stack
Absorber
Flue Gas
Recycle Stream
Saturated Na_2CO_3 Solution
Recirculation Tank
Na_2CO_3
Na_2CO_3 Slurry Storage Tank
Make-up water
Feed Water
Aqueous Waste To Treatment And Disposal

Figure 2.1-1. Process flow diagram for a sodium scrubbing system using soda ash slurry storage.

solution in the scrubber. The scrubber effluent flows (usually by gravity) to a recirculation tank where it is mixed with make-up reagent and water. If the reagent is in the form of NaOH, it is typically added as a 50 weight percent solution. If the reagent is Na_2CO_3, it is usually added as a saturated solution.[1,2] The aqueous reactions that take place in the scrubber and, to a greater extent, in the recirculation tank are:

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O \qquad (2.1\text{-}1)$$

or

$$Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2 \qquad (2.1\text{-}2)$$

and

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3 \qquad (2.1\text{-}3)$$

$$SO_2 + H_2O \longrightarrow H_2SO_3 \qquad (2.1\text{-}4)^3$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \longrightarrow Na_2SO_4 \qquad (2.1\text{-}5)$$

The residence time in the tank is typically three to four minutes. The aqueous solution leaving the recirculation tank contains primarily NaOH, Na_2CO_3, Na_2SO_3, $NaHSO_3$, H_2SO_3, and Na_2SO_4. Most of this stream is recycled to the scrubber, while a small fraction is bled for treatment and disposal.[4] This wastewater stream may be treated on-site by oxidation to reduce chemical oxygen demand (COD) and to reduce the potential for SO_2 re-emissions. This stream may also be allowed to settle in order to filter out fly ash and other insoluble compounds. Disposal of the wastewater stream is handled in one of several ways: evaporation ponding, deep-well injection, or discharge to a sewer, river, or ocean.[5]

The system's operation is monitored by the specific gravity and pH of the recirculation tank. In some systems, the specific gravity is controlled by the addition of make-up water. It determines both the buffering capacity of the scrubbing solution and the flow rate of the blowdown stream. The higher the specific gravity, the greater will be the buffering capacity of the solution and the lower will be the blowdown flow rate.[3] The pH is controlled by the addition of sodium reagent. If, for example, the process experiences a transient increase in SO_2 loading, then the pH in the recirculation tank will drop. This, in turn, signals the addition of make-up reagent to re-establish the pH to normal. Make-up water and blowdown flow rates will then both be increased to maintain the set-point value of the specific gravity.

2.1.1.2. Factors Affecting Performance. The major operating variables affecting scrubber performance are the pH and total sulfite concentration (TSC) of the scrubbing solution. The pH primarily affects SO_2 removal efficiency while TSC affects this as well as reagent consumption (for those systems not using an oxidation system for wastewater treatment) and transient performance. Other variables affecting scrubber performance are absorber type and L/G ratio. Each of these factors will be discussed in this section.

pH

The pH of the scrubbing liquor is determined primarily by the ratio of Na_2SO_3 and $NaHSO_3$. Since HSO_3^- is a weak acid (with a pKa of 7.45 at 50°C), the greater the $Na_2SO_3/NaHSO_3$ ratio is the higher the pH of the scrubbing liquor will be. According to Figure 2.1-2, raising the pH will lower the equilibrium SO_2 partial pressure of the scrubbing liquor which will in turn increase the driving force for SO_2 absorption.[6,7] This means that if all other design and operating parameters are held constant, increasing the pH of the scrubbing solution will increase the SO_2 removal efficiency of the scrubbing system.

The pH of the scrubbing solution is controlled simply by adding reagent to the recirculation tank (see Figure 2.1-1). Typically, the pH of the scrubbing solution is maintained around 7.0, which means that the $Na_2SO_3/NaHSO_3$ ratio is approximately 1:2.[8] At this pH, the equilibrium partial pressure is less than 20 ppmv for most sodium scrubbing solutions.[7] Since inlet concentrations of SO_2 range from 1,000 to 3,000 ppmv, the theoretical SO_2 removal efficiency is greater than 95 percent. Due to the reactiveness of dissolved SO_2 in aqueous sulfite solutions and the mass transfer capabilities of most absorber designs, these equilibrium values are

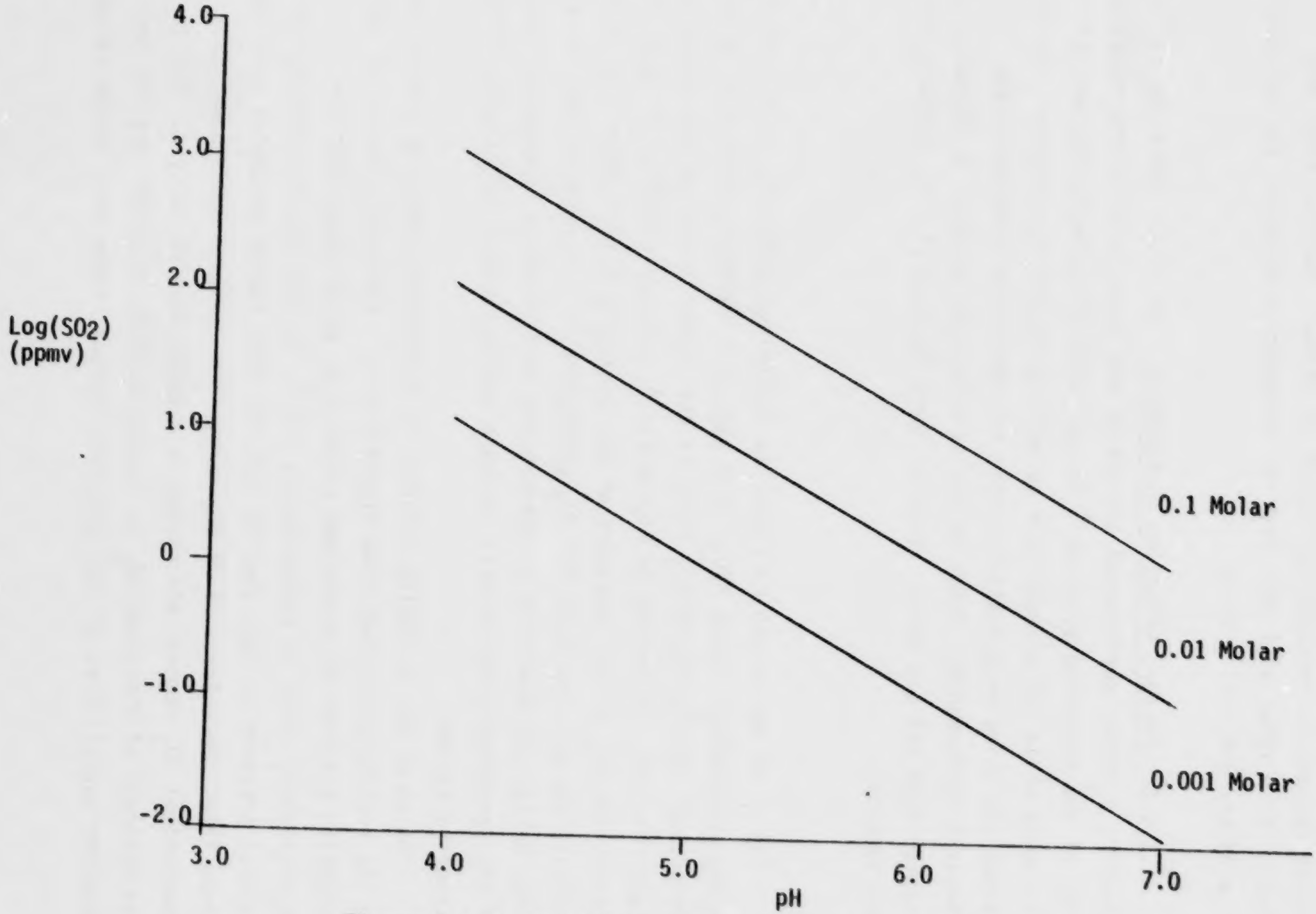


Figure 2.1-2. Equilibrium Partial Pressure of SO_2 Over Aqueous Sodium Sulfite Solutions[7]

approximated in practice. Commercially operating systems have consistently reported SO_2 removal efficiencies greater than 95 percent (see Section 2.1.1.6).

Total Sulfite Concentrations (TSC)

The total sulfite concentration (TSC) is defined as the sum of all SO_3^{-2} and its corresponding cations. For the sodium scrubbing liquor, this includes primarily Na_2SO_3 and $NaHSO_3$. It should be noted that SO_4^{-2} will also be dissolved in the scrubbing solution typically in a ratio of 1:3 relative to the sulfite species.[9] Sodium sulfite and sulfate are the primary dissolved species and together comprise the total dissolved solids (TDS) of the scrubbing solution. Sulfate is a very stable species and has little effect on scrubber performance except when it becomes so concentrated that it can promote precipitation of the sulfite species and significantly reduce SO_2 removal efficiency.

Figure 2.1-2 shows that as the TSC increases, the equilibrium SO_2 back pressure will also increase. For example, using the range observed for commercially operating systems, 0.01M to 1.7M, the SO_2 partial pressure will vary from 0.11 ppmv to 19 ppmv within this range at a pH of 7.0 and at 50°C. Assuming that all other operating and design parameters remain constant, the SO_2 removal efficiency will theoretically decrease as TSC increases. However, when compared to inlet SO_2 partial pressures of 1,000 to 3,000 ppmv, this 170-fold change in equilibrium exit partial pressure does not significantly affect the overall SO_2 removal efficiency. This fact has been substantiated by commercially operating systems which have shown no trend in SO_2 removal efficiency as a function of TSC.[10]

Although increasing TSC may reduce SO_2 removal efficiency by a small degree, it can significantly improve transient performance by stabilizing pH.[11] Since HSO_3^- is a weak acid, $NaHSO_3$ and Na_2SO_3 serve as a buffer in the scrubbing solution. The higher their concentrations are, the greater the buffering capacity of the scrubbing liquor will be. Scrubbers operated in the concentrated mode (conventionally defined as TDS levels exceeding five weight percent) will typically have an inlet pH of 7.0 - 7.5 and an outlet pH of 6.5 - 7.0.[8,12] On the other hand, scrubbers operated in the dilute mode (conventionally defined as TDS levels less than or equal to 5 weight percent) have an inlet pH of 9-10 and an outlet of pH of 4-5.[12]

Buffering is important because it increases reliability and improves transient performance. At pH's above 8.0, the likelihood of calcium scaling is high. Within most sodium scrubbing loops there is some background Ca^{+2} (e.g. from make-up water or ash leachate) which will combine with available sulfite and sulfate ions. At pH's above 8.0, $CaSO_3$ and $CaSO_4$ will precipitate out of solution and cause scaling. Sometimes this scaling will lead to plugging, especially in the recirculation lines and spray nozzles.[13] As a result, the SO_2 removal efficiency can be impaired; in the extreme cases, the unit will have to be shut down and cleaned. At low pH's, substantial corrosion of the scrubber, tank, and pipe internals can occur, especially if the scrubbing solution has a high chloride ion concentration. This corrosion will increase the maintenance costs of the scrubbing unit and decrease the scrubber's reliability.

Buffering serves another function in that it helps to prevent large pH fluctuations from occurring, even when inlet SO_2 concentrations vary dramatically, as is typical of industrial boiler operation. This insures relatively constant outlet SO_2 concentrations or, in other words, good transient SO_2 removal performance.

Absorber Design

The design of an absorber determines its mass transfer characteristics and thus SO_2 removal capabilities. Absorber designs can be grouped into three categories: open vessels, vessels with internals, and combinations of the two. Open vessel absorbers, such as venturi scrubbers, spray towers, and liquid jet eductors, rely on a combination of high gas- and liquid-side pressure drops to provide adequate mass transfer. Vessels that have internals, such as packed beds and tray towers, rely primarily on solid internal surface area for absorption. Combination absorbers, such as disc and donut contactors and spray baffles, use a combination of the characteristics employed by both open vessels and vessels with internals.

Table 2.1-1 summarizes SO_2 removal efficiencies for these three categories of absorbers, as reported by plants, vendors, and governmental agencies for approximately 290 scrubbers. Included also in Table 2.1-1 are the typical values for the absorbers' gas- and liquid-side pressure drops as well as their typical liquid-to-gas ratios (L/G's). A high gas-side pressure drop assures adequate mixing and a high liquid-side pressure drop assures not only an adequate liquid-flow rate but sufficient atomization as well. The L/G will be discussed further under its own sub-heading, and the applicability and reliability of each absorber type will be discussed in their respective sections.

Table 2.1-1 provides vendor, plant and government data for approximately 290 sodium scrubbers. The average SO_2 removal efficiency for the seven scrubber types in the table was 93.9 percent. The standard deviation was 3.9 percent.[5] (Actual emissions as determined by EPA testing methods alone are provided in Section 2.1.1.6). As shown by the table, the open vessel category has reported the second highest SO_2 removal efficiency of the three absorber categories. For the approximately 115 scrubbers within this category, the average SO_2 removal efficiency was 93.3 percent. In general, open vessels have high liquid-side pressure drops to atomize the scrubbing solution. Atomization produces small droplets with high surface area/volume ratios.[16] The gas-side pressure drop varies a great deal within this category. Spray towers, for example, have very low gas-side pressure drops to provide a low velocity gas. This low velocity provides high residence times and prevents re-entrainment of the liquor droplets. It should be noted that these low velocities may produce laminar flow in small diameter towers. Therefore, SO_2 removal efficiencies may be low for small spray tower systems.[17] Venturi scrubbers, on the other hand, have relatively high gas-side pressure drops to cause turbulent mixing. In these scrubbers, SO_2 removal efficiency improves as gas velocity increases.

The average SO_2 removal efficiency for approximately 50 tray towers was 90.6 percent. Tray towers, too, operate with some atomization, and therefore the liquid side pressure drop is moderate. Gas-side pressure drops are relatively high because of the trays. Towers with two trays are

TABLE 2.1-1 PREDOMINANT SODIUM SCRUBBING ABSORBER TYPES WITH THEIR TYPICAL SO_2 REMOVAL EFFICIENCIES AND OPERATING PARAMETERS

Absorber Category	Absorber Type	Fuel Sulfur Range (Wt. %)	SO_2 REMOVAL EFFICIENCY (%)			TYPICAL OPERATING PARAMETERS[d]			Applicability[e]
			Actual[a]	Guaranteed[b]	Theoretical[c]	Gas-side ΔP (in. H_2O)	Liquid-side ΔP (psig)	L/G (gal/1000 acf)	
Open Vessels	Venturi scrubbers	1.0-2.5	91.6[f](5.3)[g]	NA[h]	90-95	8-20	25	10	7.0
	Spray towers	1.1-1.7	88.9(4.9)	90	95-99	1.5-2.5	75	30-50	3.4
	Liquid jet eductors	1.0-2.4	94.2(3.3)	91.9	90-99	0.5-1.0	40	50-120	29
Vessels with Internals	Tray absorbers (2 stage) (3 stage)	0.7-5.5	75-90 (NA) 90.6(3.3)	NA	NA 95-97	8-12	30	20	17
	Packed bed	1.7	73.0(DNA)[i]	NA	95-99	2	nominal	1-10	11
Combination	Spray baffle	0.6-6.0	96.6(0.8)	95.0	95-99	5	30	30	32
	Disc and Donut contactor	1.0	95.0(DNA)	95.0	95-99	5	NA	10-20	0.7
			93.9[j](3.9)						

---

[a] Actual values are those reported by vendors, plants and governmental agencies.[5]

[b] Guaranteed values represent those guaranteed by vendors.[5]

[c] Theoretical values are those reported in literature.[13-15]

[d] Typical operating parameters are those compiled from vendors, plants, and literature in References 13-28.

[e] Applicability represents the percent that each absorber type comprises of the total 292 scrubbers that specified absorber types in the sample population. The sample population is located in Table 2.1-2 and lists 356 scrubbers in all.

[f] These values denote averages as determined in Reference 3.

[g] These values denote standard deviations as determined in Reference 3.

[h] NA = Not Available

[i] DNA = Does not apply. There was only one source of information and therefore calculation of the standard deviation was meaningless.

[j] Average SO_2 removal efficiencies for all scrubbers except for packed beds.[3]

not expected to achieve SO_2 removal efficiencies as high as the other absorber types.[29] Only one source reported using a packed bed and this obtained 73 percent removal.[30] However, as shown by the theoretical values, it is expected to have a much higher SO_2 value. Since the data were taken in 1973 when the emission limits were less-than-stringent, it is believed that this figure does not represent the performance of packed beds under typical operating conditions.

Those absorbers combining the features of the previous two categories have demonstrated the highest SO_2 removal efficiencies. For the approximately 90 spray baffles within the sample, an average of 96.6 percent SO_2 removal efficiency has been achieved with a standard deviation of less than one percent.[5] For the two disc and donut contactors, the efficiency has averaged 95 percent.[5] The spray baffle absorber combines a unique spiral mixing technique along with a moderate liquid-side pressure drop for atomization and a moderate gas-side pressure drop.[3] In addition, it provides solid surface area on the baffles themselves for mass transfer. The disc and donut contactor provides solid surface area as well. Mixing, too, is achieved with a baffle-type arrangement.[31]

Liquid-to-gas ratio

The liquid-to-gas ratio (L/G), measured in gal/10^3 acf, also affects SO_2 removal efficiencies. In general, as the L/G is increased the SO_2 removal capabilities will increase up to the flooding point of the scrubber.[15] This depends on the type of absorber and the degree to which the gas- and liquid-side pressure drops are increased to accommodate the increased liquid flow. Once the desired SO_2 removal efficiency is specified for a particular absorber, the L/G is set as well. Table 2.1-1 provides typical L/G's for the seven predominant absorber types for SO_2 removal efficiencies at or above 90 percent. Although there are exceptions, in general, vessels with internals require the lowest L/G, followed by combination type absorbers, and then by open vessels. In addition, those absorbers using greater degrees of atomization will, in general, require higher L/G's than those that don't.

It should be noted that L/G's are lower for sodium-based systems than for calcium-based systems. This is primarily because sodium is much more soluble in water than calcium and thus requires less water for dissolution. As shown by Table 2.1-1, except for liquid jet eductors, L/G's for sodium-based systems range from 1-50 gal/10^3 acf. For calcium-based systems (exclusive of Thiosorbic lime and Thiosorbic limestone), they range from 60 to 120 gal/10^3 acf.

2.1.1.3 Applicability to industrial boilers. The March 1982 BID indicated that sodium scrubbing was applicable only to very few types of plants. These plants had either an inexpensive reagent source or a readily available disposal technique, or both. Installation at other industrial boiler sites was assumed to be limited because of the predicted zero discharge requirement and because of the prohibitive costs of treating the waste stream (see Sections 4.2.1 and 7.2.1 of the BID). However, about 98 percent of the estimated 680 wet FGD systems installed on industrial boilers are sodium scrubbing systems (see Table 2.1-2).[5] They represent at least 80 percent of all industrial boiler wet FGD systems that treat flue gas from boiler size equivalents (BSE)* greater than 100 x 10^6 Btu/hr. Even after eliminating what the BID considered as "special" applications (such as oil field steam generators, paper mills, soda ash, and textile plants) sodium scrubbers represent at least 70 percent of the total wet FGD systems currently operating.[5] These data suggest that the assumptions set forth in the BID and ITAR should be investigated and revised where necessary. A review of some of these assumptions is presented below.

Zero Discharge Requirement

The previous analysis assumed that zero wastewater discharge requirements would restrict the use of sodium FGD systems. In some areas of the country this will be the case. For example, in California and in the

---

*Boiler size equivalent is used instead of boiler size because in many cases more than one boiler is ducted to a common scrubber.

TABLE 2.1-2. TABLE OF SODIUM SCRUBBING SYSTEMS [5]

Company/ Location	Start-up Date	Vendor	Absorber Type[a]	Fuel		Boiler Size Equivalent[c] (10^6 Btu/hr)	Number of FGD Units	%SO_2 Removal[d]		Waste Disposal Method
				Type[b]	%S			Actual	Guaranteed	
General Motors St. Louis, MO	1972	A.D. Little	TA	C	3.2	313	2	90	NA	Oxidation/neutralization/ sewer
Dayton, OH	1974	Entoleter	VG	C	0.7-2.0	82	1	86	NA	Clarify/adjust PH/sewer
Tonawanda, NY	1975	FMC	VS	C	1.2	84	4	90	NA	Aeration/treatment plant
Pontiac, MI	1976	GM	TA	C	0.8	188 250	1 1	NA	NA	Dewatered/landfill
St. Regis Paper Cantonment, FL	1973	Neptune/Airpol	NA	B,O	<1.0	375	1	80-90	NA	Clarification/aeration
Texaco San Ardo, CA	1973	Ceilcote	PB	O	1.7	70 200 30	25 2 5	73	NA	NA
	1979	Ducon	ST	O	1.7	75	3	95	NA	NA
	1982	Andersen 2000	SB	O	3.2	50	17	97	95	NA
Santa Monica, CA	1980	Thermotics	NA	O	3.5	NA	1	98	NA	NA
American Thread Marion, NC	1974	W.W. Sly Manufacturing	TA	C	<1.0	108	2	70-90	None	pond
Mobil Oil San Ardo, CA	1974	In-house	TA	O	2-2.5	22 50	20 8	90	NA	pond
	1981	NA	NA	O	1.66	50	1	95.8*	NA	NA
	1981	NA	NA	O	1.61	22	1	94.4*	NA	NA
	1981	NA	NA	O	1.39	50	1	96.8*	NA	NA
	1981	NA	NA	O	1.65	50	1	90.7*	NA	NA
	1982	NA	NA	O	1.56	22	1	87.5*	NA	NA
	1982	NA	NA	O	1.58	50	1	89.7*	NA	NA
	1982	NA	NA	O	1.47	22	1	93.9*	NA	NA
Kern Co., CA	1982	NA	NA	O	1.0	23	1	91*	NA	NA
	1982	Heater Technology	NA	O	1.0	27.5	1	89*	NA	NA
Buttonwillow, CA	1979	Heater Technology	LJE	O	1.1	64	7	85	NA	pond
McKitterick, CA	1979	Heater Technology	LJE	O	1.1	50	7	95	90	NA
	1980		LJE	O	1.1	50	2	96	96	NA

TABLE 2.1-2. TABLE OF SODIUM SCRUBBING SYSTEMS (Continued)

Company/ Location	Start-up Date	Vendor	Absorber Type[a]	Fuel		Boiler Size Equivalent[c] (10^6 Btu/hr)	Number of FGD Units	$\%SO_2$ Removal[d]		Waste Disposal Method
				Type[b]	%S			Actual	Guaranteed	
Taft, CA	1980	Heater Technology	LJE	0	1.2	25	2	96	95	NA
Bakersfield, CA	1980	Heater Technology	LJE	0	1.2	25 50	8 3	95	90	NA
Belridge, CA	1980 1981 1982	Heater Technology	LJE LJE LJE	0 0 0	1.0 1.0 1.2	50 50 25	10 3 2	95	90	NA
Georgia Pacific Crosett, Ak	1975	Neptune/ Airpol	VS	B,C,0	1.5-2	650	1	80	NA	Sewer
Great Southern Paper Cedar Springs, GA	1975	Neptune/ Airpol	VS	B,C,0	1-2	1650	2	85-90	NA	Pond
ITT Rayonier Fernandina Beach, FL	1975	Neptune/ Airpol	VS	B,0	2-2.5	400 340	1 1	80-85	NA	Wastewater treatment/pond
Mead Paperboard Stevenson, AL	1975	Neptune/ Airpol	TA	0	1.5-3	100	1	95	NA	To digester in pulping process
Husky Oil San Ardo, CA	1976	Heater Technology	LJE	0	1.4	25	1	85	80	NA
Texasgulf Granger, WY	1976	Swemco	TA	C	0.75	340	2	90	NA	Deep well injection pond
Nekoosa Paper Ashdown, AK	1976	Neptune/Airpol	VS	C	1-1.5	700	2	90	NA	To digester in pulping process
FMC Green River, WY	1976	FMC	DD	C	1.0	400 800	1 1	95	95	Salt pond
Alyeska Pipeline Valdez, AK	1977	FMC	NA	0	<0.1	NA	1	96	NA	Oxidation/dilution
Getty Oil Bakersfield, CA	1977 1979	FMC In-house In-house	TA TA NA	0 0	1.1 1.1	300 450 500	1 5 4	90 96 96	NA NA NA	Deep well injection pond Deep well injection pond Pond
Santa Maria, CA	1977	In-house	NA	0	4.0	NA	1	94	NA	NA
McKittrick, CA	1980	Heater Technology	LJE	0	1.1	75	1	96	95	NA

TABLE 2.1-2. TABLE OF SODIUM SCRUBBING SYSTEMS (Continued)

Company/ Location	Start-up Date	Vendor	Absorber Type[a]	Fuel		Boiler Size Equivalent[c] (10^6 Btu/hr)	Number of FGD Units	%SO_2 Removal[d]		Waste Disposal Method
				Type[b]	%S			Actual	Guaranteed	
Fellows, CA	1980	Heater Technology	LJE	0	1.1	75	1	95	90	NA
Taft, CA	1982	Andersen 2000	SB	0	1.1	37.5	2	96	95	Hauling to secure site
Kern Co., CA	1982	NA	NA	0	1.0	375	2	98*	NA	NA
Union Oil Guadalupe, CA	1978	Andersen 2000	SB	0	2.8	50	2	98	95	Hauling to secure site
		Heater Technology	LJE	0	2.4	25	2	90	80	NA
	1980	Heater Technology	LJE	0	2.4	50	1	96	95	NA
Kern Co., CA	1978	Andersen 2000	SB	0	1.1	50	5	96	95	Hauling to secure site
Taft, CA	1979	Heater Technology	LJE	0	1.1	25	1	95	90	NA
Mckittrick, CA	1980	Heater Technology	LJE	0	1.1	50	7	96	95	NA
	1981	Andersen 2000	SB	0	0.7-1.2	NA	4	95	NA	NA
Belridge Oil McKittrick, CA	1978	Heater Technology	LJE	0	1.5	50	1	95	80	NA
			LJE	0	1.1	50	2	90	NA	Waste water treatment/pond
	1979	CE Natco	ST	0	1.1	50	1	90	NA	NA
Elf Aquitaine Kern Co., CA	1978	Andersen 2000	SB	0	1.1	50	1	96	95	Hauling to secure site
	1983	Andersen 2000	SB	0	1.1	50	1	96	95	Hauling to secure site
Kerr-McGee Trona, CA	1978	CEA	TA	0	0.7-5.5	750	2	98*	NA	Salt pond
Chevron Bakersfield, CA	1978	Koch	TA	0	1.1	130	3	90	NA	Pond/waste treatment
	1979	Koch	TA	0	1.1	300	2	90	NA	Pond/waste treatment
	1980	Neptune/Airpol	NA	0	NA	50	11	95	NA	NA
Maricopa, CA	1979	Heater Technology	LJE	0	1.1	50	1	96	95	NA
Kern Co., CA	1980-1982	Andersen 2000	SB	0	1.3	50	7	97	95	NA
	1982	NA	NA	0	0.8	437.5	1	96*[f]	NA	NA
	1982	NA	NA	0	1.04	462.7	1	96*[f]	NA	NA
	1982	NA	NA	0	1.2	NA	1	97*[f]	NA	NA

TABLE 2.1-2. TABLE OF SODIUM SCRUBBING SYSTEMS (Continued)

Company/ Location	Start-up Date	Vendor	Absorber Type^a	Fuel Type^b	Fuel %S	Boiler Size Equivalent^c (10^6 Btu/hr)	Number of FGD Units	%SO_2 Removal^d Actual	%SO_2 Removal^d Guaranteed	Waste Disposal Method
General American Oil										
Taft, CA	1978	Andersen 2000	SB	0	1.2	50	1	98	95	Hauling to secure site
	1982	Andersen 2000	SB	0	1.2	75	1	98	96	Hauling to secure site
Gulf Oil										
Lost Hills, CA	1978	Andersen 2000	SB	0	1.2	50	2	97	95	Deep well injection
Kern Co., CA	1982	Andersen 2000	SB	0	0.6	55.2	1	95*	NA	NA
		Andersen 2000	SB	0	1.0	25	1	99.5*	NA	NA
		NA	NA	0	1.2	30	1	93.5*	NA	NA
		Andersen 2000	SB	0	1.3	25-50	5^h	97	95	Hauling to secure site
Sun Production Co.										
Fellows, CA	1979	CE Natco	ST	0	1.4	50	1	85	NA	Pond
Newhall, CA	1979	CE Natco	ST	0	1.3	NA	2	85	NA	NA
Oildale, CA	1979	CE Natco	ST	0	1.2	50	2	85	NA	Pond
Phillip Morris										
Chesterfield, VA	1979	Flakt	ST	C	NA	237	1	NA	90	Aeration
Tenneco Oil										
Bakersfield, CA	1979	Andersen 2000	SB	0	1.0	50	1	99	95	Hauling to secure site
	1982-	Andersen 2000	SB	0	1.0-1.6	50-150	9^g	96-98	95	Hauling to secure site
	1983	NA	NA	0	1.04	261.8	1	99.4*	NA	NA
Green River, WY	1982	Flakt	NA	C	1.5	300	2	93	NA	Pond
Shell Oil Co.										
Coalinga, CA	1980	Ducon	NA	0	0.6	NA	2	90	NA	NA
	1981	Ducon	NA	0	0.6	NA	1	90	NA	NA
Bakersfield, CA	1981	Neptune/Airpol	NA	0	1.1	50	2	96.4	NA	NA
						100	2			
						180	1			
						200	1			
	1983	NA	NA	0	0.80	100	1	99.2*	NA	NA
		NA	NA	0	0.80	100	1	98.6*	NA	NA
		NA	NA	0	0.79	52	1	98.8*	NA	NA
		NA	NA	0	0.79	50	1	99.8*	NA	NA
Kernridge Oil										
McKittrick, CA	1980	Andersen 2000	SB	0	1.2	50	1	95	95	NA

TABLE 2.1-2. TABLE OF SODIUM SCRUBBING SYSTEMS[1] (Continued)

Company/ Location	Start-up Date	Vendor	Absorber Type[a]	Fuel		Boiler Size Equivalent[c] (10^6 Btu/hr)	Number of FGD Units	$\%SO_2$ Removal[d]		Waste Disposal Method
				Type[b]	%S			Actual	Guaranteed	
Kern Co., CA	1982	CE Natco	VS	0	1.0	62.5	9	96*	NA	NA
		Ducon	NA	0	1.1	125	1	96*	NA	NA
		CE Natco	NA	0	0.85	62.5	1	97*	NA	NA
		CE Natco	VS	0	1.10	125	1	99*	NA	NA
		CE Natco	NA	0	1.10	62.5	1	96*	NA	NA
		CE Natco	NA	0	1.0	NA	1	94*	NA	NA
Santa Fe Energy Fellows, CA	1980	Heater Technology	LJE	0	1.2	50	6	96	95	NA
						25	1			
Coalinga, CA	1981	Heater Technology	LJE	0	0.8	50	5	96	95	NA
	1982	Heater Technology	LJE	0	0.8	50	10	96	95	NA
Bakersfield, CA	1982	NA	NA	0	1.52	50	1	97.5*	NA	NA
		NA	NA	0	1.52	50	1	96.2*	NA	NA
Grace Petroleum Pismo Beach, CA	1982	Thermotics	NA	0	1.2	NA	4	98	NA	NA
Sun Oil Kern Co., CA	1980-1981	Andersen 2000	SB	0	1.1	25-100	4[f]	96	95	Hauling to secure site
Miles Labs Clifton, NJ	1981	Andersen 2000	SB	0	2.8	42.8	1	96	95	Sewer
Struthers Oil & Gas Red Lodge, MT	1981	Andersen 2000	SB	0	2.2	17.8	1	98	95	NA
St. Joe Paper Port St. Joe, FL	1982	Neptune/Airpol	NA	B,O	NA	NA	1	NA	NA	NA
Aminoil Huntington Beach, CA	1982	Andersen 2000	SB	0	2.0	50	13	96	95	NA
Occidental Petroleum Taft, CA	1982	Andersen 2000	SB	0	1.1	50	2	97	95	NA
Exxon Kern Co., CA	1982	Andersen 2000	SB	0	1.2	25	1	97	95	NA
Petro Lewis Kern Co., CA	1982	NA	NA	0	0.8	62.5	1	99*[f]	NA	NA
		CE Natco	NA	0	1.15	62.5	1	95*[f]	NA	NA
	1983	Thermotics	NA	0	1.02	62.5	1	98*[f]	NA	NA

TABLE 2.1-2. TABLE OF SODIUM SCRUBBING SYSTEMS (Continued)

Company/ Location	Start-up Date	Vendor	Absorber Type[a]	Fuel Type[b]	%S	Boiler Size Equivalent[c] (10^6 Btu/hr)	Number of FGD Units	$\%SO_2$ Removal[d] Actual	$\%SO_2$ Removal[d] Guaranteed	Waste Disposal Method
USS Tenneco Chem Pasadena, TX	1983	Andersen 2000	SB	OW	NA	300	2	NA	95	NA
Tosco Petroleum Kern Co., CA	1983	Andersen 2000	SB	0	1.1	25	1	95	NA	NA
Marathon Oil Kern Co., CA	1983	Andersen 2000	SB	0	1.2	50	1	97	95	Hauling to secure site
Garwood Paper Garwood, NJ	1983	Andersen 2000	SB	0	4.2	50	1	98	95	Oxidation/sewage
American Petrofina Big Spring, TX	1983	Andersen 2000	SB	0	6	240	1	NA	96	Oil field injection
Bradford Dyeing Assoc. Westerly, RI	1983	Andersen 2000	SB	0	4	214	1	NA	95	NA
Optimum Energy Kern Co., CA	1983	Andersen 2000	SB	0	1.2	300	2	NA	96	Hauling to secure site

[a] TA = tray absorber; LJE = liquid jet eductor; DD = disk and donut contactor; SB = spray baffle; VS = venturi scrubber; ST = spray tower; PB = packed bed; VA = vane gage.

[b] C = coal; O = oil; B = bark; PC = petroleum coke; OW = organic waste.

[c] Boiler size equivalent represents the heat load applied to each scrubber.

[d] The values for percent SO_2 removal have been reported by either the FGD system operator or by the vendor. These values may or may not be obtained by approved EPA methods (* = the starred values are known to have been obtained by EPA methods).

[e] NA = not available.

[f] Calculated assuming HHV = 18,500 Btu/lb.

[g] It is assumed that a 50, 100 and 150 MM Btu/hr boiler are eached served by 3 FGD units.

[h] It is assumed that there are 2 25 MM Btu/hr units and 3 50 MM Btu/hr units each served by one scrubber.

[i] It is assumed that there are 1 25 MM Btu/hr unit, 2 50 MM Btu/hr units, and 1 100 MM Btu/hr unit each served by one scrubber.

Southwest where the surface and ground water supplies have a high background salinity and where crops are especially sensitive to high TDS water, sodium blowdown streams can not, in most cases, be discharged into the local water systems either directly or via a local sewage plant.[32] Similarly, it is doubtful that the blowdown could be discharged in North Dakota's water supplies since they already have high background sulfate concentrations.[33] In these cases, the zero discharge requirement would probably have to be met, not because of national regulations but because of local restrictions.

Implicit in the assumption that the sodium scrubber wastewater would not be allowed to be discharged to surface waters and sewers are the assumptions that the aqueous waste from sodium scrubbers significantly impacts the quality of the receiving water body and that the zero discharge laws which were being considered in the late 1970's would become a reality by 1985. However, two of the waste stream characteristics which were previously thought to be deleterious already comply with current water regulations or can be made to do so with minimal treatment. The typical pH levels of sodium waste streams comply with the water quality standards set forth in the 1976 Quality Criteria for Water and thus do not require neutralization.[35] The blowdown stream's chemical oxygen demand (COD), due to the oxygen scavenger Na_2SO_3, can be reduced adequately by aeration.

The only potential secondary pollution concerns associated with the sodium scrubbing wastewater stream is its total dissolved solids (TDS) concentration and its trace metals concentration. In most industrial plants, the scrubber wastewater is diluted by combining it with other wastewater streams produced in the plant. The total plant effluent is not treated for TDS and is generally not treated specifically for trace metals. However, it is very likely that many of the trace metals will precipitate out as metal hydroxides and be removed along with the other suspended solids in the plant effluent.[36] Nevertheless, in most cases the receiving water body, whether it is a sewer or river, has the capacity to dilute the scrubber wastewater that is discharged with the plant effluent to such a degree that water quality impacts are negligible.[34] If the impacts had been significant, then the local water authorities would not have issued permits for the various sodium scrubbing streams that are currently being discharged. Information collected in this update show that 14 plants using sodium scrubbers are known to discharge their wastewater either to a sewer or directly to a river.[5] One sodium scrubbing vendor claims to know of 30 such plants that discharge to a sewer.[3]

That the zero effluent discharge has not become a reality is substantiated by these numerous plants that are discharging to surface waters. Currently, there are no plans by the Effluent Guidelines Division to regulate the sodium scrubbing wastewater itself.[37] Furthermore, a similar stream, the scrubber sludge stream, is not specifically regulated under the effluent standards for the Steam Electric Point Source Category.[38]

One further secondary pollution impact that might limit the use of sodium scrubbers but was not discussed in the BID or ITAR is the potential for SO_2 re-emission due to the back pressures illustrated in Figure 2.1-2.[6,7] The concern over SO_2 re-emissions is that the overall SO_2 removal efficiency of sodium scrubbers can be substantially reduced. An extensive study of this issue has shown that this potential can, for all practical purposes, be eliminated by converting all of the sulfite to sulfate in a well-operated oxidation tank.[7] Conversion to the very stable sulfate will also minimize reduction of sulfur to hydrogen sulfide gas in sewer systems.[39]

Presentation and Analysis of Applicability Data

Table 2.1-2 presents a list of approximately 360 sodium scrubbers, representing approximately half of the estimated 670 sodium scrubbers in use today. This figure of 670 was derived from one vendor's approximation of its market share and the number of units it had sold.[3,5] Specifically, this vendor estimates that its 233 systems represent 30-40 percent of the sodium scrubbers applied to industrial boilers.[3] Although this claim alone should not be used in determining the total number of sodium scrubbers, it is substantiated by the following information:

- Only 92 of this vendor's units are accounted for in the sample population. This represents less than 30 percent of those scrubbers within our sample for which a vendor's name was given.[5]
- If the remaining 141 of this vendor's scrubbers are added to the number of sodium scrubbers in the sample population, then approximately 500 would be accounted for.
- Several major vendors either did not respond or were not contacted. Their recent installations, therefore, are not accounted for in the sample. The 500 figure mentioned above should therefore be conservative.
- One official from Kern County estimates that there are about 1000 steam generators and virtually all have sodium scrubber.[40] It should be noted, though, that a single scrubber will, in many cases, treat the flue gas from more than one steam generator. Nevertheless, it suggests that there are many sodium scrubbers in the field today that are not accounted for by the sample in Table 2.1-2.

Other pertinent information presented in Table 2.1-2 include actual and guaranteed SO_2 removal efficiency, start-up date, boiler size equivalent, fuel type and sulfur content, and wastewater disposal technique. Those scrubbers that were found to have been shut-down since the last survey were deleted from the list. Within this revised sample, California scrubbers comprise roughly 90 percent of the total sodium scrubber population, with the remaining 10 percent fairly evenly distributed throughout 15 other states. Sixty-one percent of the California scrubbers are located in Kern County.[5]

Tables 2.1-3, 2.1-4, 2.1-5, and 2.1-6 were derived from Table 2.1-2 and provide further analyses of the information contained within it. Table 2.1-3 presents the population of sodium scrubbers by application. It also categorizes these applications into three boiler size equivalents: 0 - 100 x 10^6 Btu/hr, 100 - 250 x 10^6 Btu/hr, and greater than 250 x 10^6 Btu/hr. The most pertinent conclusions to be derived from this table are listed below.

- Sodium scrubbers installed to treat flue gas from oil field

TABLE 2.1-3 POPULATION OF SODIUM SCRUBBERS BY APPLICATION[a,b]

Application	Boiler Size Equivalent (MMBTU/hr)						Total Number Within Sample		Percent of Sodium Scrubber Sample	
	0 - 100		100 - 250		250+					
	Before 1980	After 1980	Before 1980	After 1980	Before 1980	After 1980	Before 1980	After 1980	Before 1980	After 1980
Paper mill		1	1		8		9	1	6.3	0.5
Textile mill			2	1			2	1	1.4	0.5
Oil generators field	99	161	5	15	12	7	116	183	81.1	94.3
Refinery		2		1		2	0	5	0	2.6
Soda Ash					6	2	6	2	4.2	1.0
Other Industrial	5	2	2		3		10	2	7.0	1.0
Total	104	166	10	17	29	11	143	194	100	100
Mean Boiler Size Equivalent[c]	50.78	46.20	153.10	137.29	547.28	337.45				

---

[a] Reference 5.

[b] The sample itself represents 96 percent of the total wet FGD systems that have been installed up to October 1983. If the estimated 670 sodium scrubbers are used, then sodium scrubbing represents about 98 percent of the total number of wet FGD systems.

[c] Mean Boiler Size Equivalent ($Q > 100$ MMBTU/hr):

Before 1980	446.21
After 1980	215.93
Overall	349.97

TABLE 2.1-4 TOTAL SO_2 TREATED BY APPLICATION FOR CURRENT SODIUM SCRUBBER SAMPLE[b,c] (1000 lb SO_2/yr)[3]

	Boiler Size Equivalent (MMBTU/hr)				Percent of SO_2 Treated by Sodium Scrubbers	
	0 - 100		$\geq$ 100			
Application	Before 1980	After 1980	Before 1980	After 1980	Before 1980	After 1980
Paper mill	1,300	1,200	85,960		35.7	1.2
Textile mill			1,900	4,500	0.8	4.8
Oil field generators	51,500	56,000	38,500	21,900	36.8	76.4
Refinery		900		8,200	0	8.9
Soda Ash			41,700	8,000	17.0	7.9
Other Industrial	3,400	900	23,700		11.0	0.9
Total	56,200	59,000	191,760	42,600	100	100

TABLE 2.1-5. POPULATION OF SCRUBBERS ON UNITS FIRING OIL, COAL AND OTHER FUELS[5]

State	Number of Units Firing Coal[a]			Number of Units Firing Oil			Number of Units Firing Other Fuels			Average Sulfur Content	
	0-100	100-250	250+	0-100	100-250	250+	0-100	100-250	250+	mean	std. dev.
Alabama					1					2.25	-
Arkansas			2						1	1.42	0.29
California				262	20	21				1.49	0.63
Florida									3	1.83	0.72
Georgia									2	1.50	0.00
Michigan		1	1							0.80	0.00
Missouri			2							3.2	0.00
Montana				1						2.2	-
North Carolina		2								1.00	0.00
New Jersey				2						3.50	0.99
New York	4									1.20	0.00
Ohio	1									1.35	-
Rhode Island					1					4.0	-
Texas					1				2	6.0	-
Virginia		1								-	-
Wyoming			6							1.08	0.34
Total	5	4	11	265	23	21	—	—	8	1.51	0.73

	Coal	Oil	Other Fuel
Percent	6	92	2
Average Sulfur Content	1.35	1.52	1.71
Standard Deviation	0.67	0.727	0.485

[a] Boiler Size Equivalent (MM Btu/hr)

[b] # reporting fuel type = 356

[c] # reporting sulfur content = 323

[d] # reporting fuel type and boiler size = 337

TABLE 2.1-6 POPULATION OF WASTE DISPOSAL METHODS OF SODIUM SCRUBBERS[5]

	Disposal Method						Treatment Method		
State	Sewer then RWB[a]	Discharge to a RWB	Ponding	Deep-well injection	Used in Plant Processes		Oxidation for COD	Removal of TSS	Dilution
Alabama					1				
Alaska							1		1
Arkansas		2					2	2	
California			21	9					
Florida		2					2	2	
Michigan	1						1	1	
Missouri	1						1		
North Carolina		2						2	
New Jersey	2						1		
New York		1					1		
Ohio	1							1	
Rhode Island		1							
Texas		1		1					
Wyoming			2	1					
Total	5	9	23	11	1	Total	9	8	1
Percent of of total	10	18	47	23	2				
Total excluding CA & WY	5	9	0	1	1				
Percent of total excluding CA & WY	31	56	0	6	6				

[a] RWB = Receiving Water Body

[b] TSS = Total Suspended Solids

generators comprise about 89 percent of all industrial boiler sodium scrubbers and about 94 percent of those installed after 1980. In addition, sodium scrubbers on oil field generators comprise about 91 percent of all wet FGD scrubbers installed after 1980.

- The overall mean BSE for sodium scrubbers is 109 x 10^6 Btu/hr. For the units greater than or equal to 100 x 10^6 Btu/hr, the overall mean BSE is 350 x 10^6 Btu/hr and since 1980 has been 220 x 10^6 Btu/hr.
- Of all the sodium scrubbers in operation today, approximately 74 percent treat BSE's less than 100 x 10^6 Btu/hr.
- The number of installations since 1980 for all applications except for oil field generators and refineries have decreased relative to those before 1980.

Although Table 2.1-3 presents useful data concerning the number of sodium scrubbers, it gives no indication of the amount or percentage of SO_2 treated. Table 2.1-4 presents the total SO_2 treated in each industrial application. This sample itself treats about 70 percent of the SO_2 treated by all wet FGD scrubbers. If all of the estimated 670 sodium scrubbers are considered, then sodium scrubbers treat approximately 82 percent of the SO_2 treated by all FGD scrubbers. Other conclusions to be derived from this table are listed below.

- Approximately 360,000 tons per year of SO_2 are currently being treated by sodium scrubbers.
- Although oil field scrubbers represent 89 percent of all sodium scrubbers, they treat only 49 percent of the SO_2 treated by all industrial boiler sodium scrubbers. For BSE's greater than or equal to 100 x 10^6 Btu/hr, they treat only 28 percent of the SO_2 treated by all sodium scrubbers above that size.
- Sodium scrubbers in paper mills and soda ash plants treated over 50 percent of the total SO_2 treated by pre-1980 installations. Post-1980 installations treat less than 10 percent. It is speculated that most if not all pre-1980 installations were retrofits.

Table 2.1-5 presents those scrubbers within our sample for which fuel type and sulfur content information were provided. It breaks down the analysis into state and BSE as well. The following are pertinent conclusions:

- The average fuel sulfur content of this sample is 1.51 weight percent with a standard deviation of 0.73. If California is excluded, the average sulfur content is 1.78 with a standard deviation of 1.23.
- Ninety-two percent of the scrubbers service boilers firing oil. When California scrubbers are ignored, only 20 percent of the remaining scrubbers service boilers firing oil and 60 percent service boilers firing coal.
- The sulfur content of the coal is about 10 percent less than that of the oil.
- There appears to be a growing demand for sodium scrubbers in refineries to treat the flue gas from process boilers firing high sulfur oil (6-8 weight percent). This trend is confirmed by a prominent sodium scrubbing vendor.[3]

Table 2.1-6 presents the population of waste disposal methods by category and by state. Thirty-nine of the 72 plants in the sample provided this information. The important conclusions are summarized below.

- About 50 percent of the plants reporting wastewater disposal procedure use evaporation ponds. However, all of these plants are located in California and Wyoming.
- Approximately 10 percent of the plants dispose of their waste in a sewer. If California and Wyoming are ignored, the sewerage option represents 31 percent.
- Approximately 20 percent of the plants use aeration to treat the scrubber wastewater prior to discharge.

Table 2.1-1 presents the distribution of scrubber types for those 290 scrubbing units within our sample that reported scrubber type. The three different categories (open vessels, vessels with internals, and combination vessels) comprise approximately an equal fraction each of the total sample population. Specifically, the open vessels comprise 39 percent; the vessels with internals comprise 28 percent, and the combination vessels comprise 33 percent. Spray baffles represent the highest percentage of the population of scrubbers; liquid jet eductors and tray towers are next. Packed beds follow these; however, the packed beds' statistic is probably a distortion of the absorber's overall representation. Unlike most of the other absorber types whose data were derived from many plants, the packed bed data came from one source. Moreover, this source made its report in 1973. Since packed beds were the most popular absorption device among the first generation scrubbers (for both sodium and calcium reagents) it is not surprising to see such a large number at one plant at that time. However, demand for these units has diminished substantially in recent years primarily because of reliability problems. Therefore, it is doubtful that they will be applied widely in the future.

Reasons for the Current Popularity of Sodium Scrubbers

The reasons for the prevalence of sodium scrubbing systems as compared to other industrial FGD systems are listed below:

- Ease of operation
- High reliability
- Relatively low initial capital costs
- Relatively low total annualized costs (for low SO_2 loadings)

The primary reason sodium scrubbers are popular is that they are relatively easy to operate, requiring little operator attention. Although reliability is a function of ease of operation, it is nevertheless a separate reason for sodium scrubbing popularity. Some industrial boiler plants must shut their whole process down if the scrubber malfunctions. In these cases, the penalty associated with process downtime may be high. In other cases, loss of the scrubbing system will require the boiler owner to burn more expensive, low-sulfur fuels. Process economics (capital and annualized costs) also substantially affect system applicability and should thus be mentioned here as well.

Since oil field generators use such a large percentage of the sodium scrubbers, a separate applicability explanation is warranted for them. There are four primary reasons for their predominance, some of which are unique to their application. First, since steam generators are remotely located, they must be able to operate without operator attention. Second, because of the strict air regulation in their areas, they must be exceptionally reliable because the generator must be shut down if the scrubber malfunctions. Third, generators are moved frequently from one oil well to the next, and sodium scrubbers are the most portable wet FGD systems. And fourth, since SO_2 loadings from oil field generators are generally low, sodium scrubbers are usually the least expensive of the FGD technologies.

2.1.1.4 Development Status. Sodium scrubbers are well demonstrated. Approximately 400 units have been installed since 1980,[5] resulting in a great deal of process refinement which has translated into reductions in cost. For example, capital costs are now approximately 40 percent of what they were five years ago.[3] As would be expected with any maturing technology, this cost reduction can be attributed both to the increased economies of high production volumes and to increased standardization. In addition, process control has become more sophisticated for sodium systems, resulting in an increase in system reliability as well as reductions in labor and maintenance requirements.

2.1.1.5 Reliability. Reliability, operability, and availability are typically used interchangeably throughout industry without any rigorous definition of each. Thus, the term "reliability" is subject to different interpretations, and in normal usage is understood to mean that a system is either "free from failure" or it is "able to function when needed." To avoid confusion, the EPA has standardized these terms by defining them quantitatively. These definitions are as follows:

Availability: Hours the FGD system was available (whether operated or not) divided by the hours in the period, expressed as a percentage.

Operability: Hours the FGD system was operated divided by boiler operating hours in the period, expressed as a percentage.

Reliability: Hours the FGD system was operated divided by the hours the FGD system was called upon to operate, expressed as a percentage.

When requesting "reliability" data from plants, reliability was the index requested and was presented to the plants as the definition above. The numbers presented in Table 2.1-7 are the values provided by various plants and vendors in response to this definition. It should be noted that no actual operating data or logs were obtained for these systems, nor were time periods of data collection specified by the plants and vendors. These data are therefore not to be taken as rigorous measures of sodium scrubbing performance. Nevertheless, because all are consistently high, they show that sodium scrubbing is exceptionally reliable. Earlier information from the EPA Industrial Boiler FGD Survey: First Quarter 1979 showed reliability figures similar to these recently acquired data. Fifteen boiler operators reported reliability and/or operability indices of between 89 and 100 percent with an average of 97.8 percent. Of the 15 responses gathered in that survey, 9 reported a 100 percent reliability and only two reported reliabilities less than 95 percent.[42]

These high reliabilities are due primarily to the simplicity of both the chemistry and design of the process. The sodium species in the recirculation stream remain in solution at the TDS concentrations and temperature ranges typically found in the operation of sodium scrubbing systems.[43] Solution scrubbing minimizes the erosion of pumps and pipes, as well as the scaling of mist eliminators all of which contribute to a substantial fraction of the downtime in calcium-based systems. Calcium, leached from coal ash and sometimes present in the make-up water itself, is the predominant precipitable species. However, its concentration generally

TABLE 2.1-7 RECENT RELIABILITY DATA FOR SODIUM SCRUBBERS

Plant or Vendor	Number of Scrubber Units	Reliability (%)
A[41]	15	99 - 99.5
B[18]	2	99+
C[25]	1	100
D[3,20]	233	98+
E[21]	5	98

is too low to cause scaling problems, even at relatively high pH's. Operating the system in the concentrated mode reduces the risk of calcium precipitation by reducing system pH. Even more importantly, the concentrated solution provides a buffer which is effective in preventing the pH excursions that can result from widely fluctuating inlet SO_2 flow rates.

In addition, a vast majority of the sodium systems operate with open vessels, or combination vessel scrubbers. Those scrubber systems that have vessels with internals are expected to have lower reliabilities. Compared to vessels with internals, open vessels increase reliability by reducing both the horizontal solid surface area available for scale formation and the residence time of the scrubbing liquid on a solid surface. These factors in turn minimize isolated pH excursions that can cause scaling and corrosion.

2.1.1.6 Emissions Data. Table 2.1-8 presents SO_2 removal efficiencies and outlet SO_2 emissions for 45 scrubbers at 18 different sites.[44] SO_2 removal efficiencies for these scrubbers ranged from 89.3 to 99.4 percent, while outlet SO_2 emissions ranged from 0.007 $lb/10^6$ Btu to 0.23 $lb/10^6$ Btu. The average sulfur content in the fuels fired at all sites was 1.30 weight percent with a standard deviation of 0.64 weight percent. For the boilers at the sites firing oil only, the average sulfur content was 1.17 weight percent with a standard deviation of 0.28 weight percent. Other relevant data in this table include the year in which the tests were performed, method of testing, absorber type, and pH of the scrubbing liquid. All but one test were performed after 1980, and all but one scrubber, which is at Site #1, operated on a boiler that fired oil. The scrubber at Site #1 treated the flue gas from a boiler firing coal that had a sulfur content of 3.64 weight percent.

Table 2.1-8a presents the results of the average SO_2 removal efficiencies and average SO_2 outlet emissions for the 45 scrubbers listed in Table 2.1-8. The average SO_2 removal efficiency was 96.2 percent with a standard deviation of 2.9 percent. However, if the data for the two tray absorber site (Site #10) are deleted, the average SO_2 removal efficiency per scrubber becomes 96.7 percent with a standard deviation of 2.3 percent. The

TABLE 2.1-8 EMISSIONS DATA FROM SELECTED SODIUM SCRUBBING FGD SYSTEMS[44]

Source (Company)	Site	Number of Scrubbers	Year of Test	Test Method	SO_2 Removal Efficiency (%)	Outlet Emissions (lb/SO_2/10^6 Btu)	Fuel Type[a]	Fuel's Sulfur Content (wt. %)	Absorber Type[b]	Scrubber Inlet pH
1	1	1	1979 -1980	CEM[d]	92.2[f]	0.20	C	3.64	TA	8.1
2	2	2	1983	EPA 8	96.6	0.055	0	1.50	LJE	NA[n]
2	3	1	1983	EPA 8	99.0[f]	0.02	0	1.14	TA	NA
2	4	1	1983	EPA 8	98.1	0.03	0	1.46	TA	NA
2	5	1	1983	EPA 8	98.1	0.03	0	1.46	SB	NA
3	6	2	1981	EPA 8	99.4[e,f]	0.026[e]	0	1.1	ST	7.0
4	7	2	1983	CEM	96.9	0.053	0	1.51	NA	NA
5	8	1	1983	CEM	99.4	0.007	0	1.04	NA	NA
6	9	4	1983	CEM	99.1	0.008	0	0.79	NA	NA
7	10	3	1981-1982	CEM	89.3[f]	0.23	0	1.60	TA[c]	7.45
7	11	4	1981-1982	CEM	95.2	0.099	0	1.43	TA	7.96
8	12	10	1982	EPA 8	96.2[f]	0.047	0	1.02	VS	NA
9	13	2	1982	EPA 8	98.0[f]	0.022	0	1.0	VS	NA
10	14	3	1982-1983	EPA 8	98.1	0.022	0	1.0	SB	NA
11	15	2	1982	EPA 8	96.5[f]	0.039	0	1.1	VS	NA
11	16	1	1982	EPA 8	95.0[f]	0.038	0	0.6	SB	NA
12	17	3	1982	EPA 8	96.2	0.058	0	1.01	NA	NA
13	18	2	1982-1983	EPA 8	90.0[f]	0.095	0	1.0	LJE	NA

[a] C = Coal: 0 = Oil.

[b] TA = Tray Absorber: VS = Venturi Scrubber: SB = Spray Baffle: ST = Spray Tower; LJE = Liquid Jeft Eductor; NA = Not Available

[c] This tray absorber was known to contain only two trays. Two try absorbers are known to have lower SO_2 removal efficiencies than those of three tray absorbers.

[d] CEM means continuous emission monitoring. At site #1, a 30-day continuous emission monitoring test was performed. At site #7-11, short-term continuous emission monitoring tests were performed.

[e] SO_2 outlet emissions were determined in lb/10^6 Btu for one scrubber only.

[f] SO_2 removal efficiency was determined from measured inlet and outlet SO_2 emissions.

[g] NA means not available.

TABLE 2.1-8a. AVERAGE RESULTS FROM SODIUM SCRUBBING SYSTEMS[44]

	SO_2 Removal Efficiencies ± Standard Deviations, in Percent	
1)	Average efficiency for all sites.	96.5 ± 2.9
2)	Average efficiency for the nine sites that measured inlet/outlet SO_2 emissions.	95.5 ± 3.6
3)	Average efficiency for all sites excluding the site with the two tray scrubber (site 10).	96.9 ± 2.3
4)	Average efficiency for all scrubbers.	96.2 ± 2.9
5)	Average efficiency for all scrubbers excluding the two tray scrubbers (Site 10).	96.7 ± 2.3
	SO_2 Outlet Emissions ± Standard Deviations, in lb $SO_2/10^6$ Btu	
1)	Average SO_2 outlet emissions for all sites,	0.060 ± 0.062
2)	Average SO_2 outlet emissions for oil-fired boiler sites	0.052 ± 0.053

TABLE 2.1-8b. SO_2 REMOVAL EFFICIENCIES BY ABSORBER TYPE[44]

Type of Absorber	Number of Scrubbers	Number of Sites	Range of SO_2 Removal Efficiency (%)
Venturi scrubber	11	2	96.3 ± 1.2
Tray Absorber[a]	7	4	96.3 ± 1.8
Spray Baffle	3	3	97.5 ± 2.3
Liquid Jet Eductor	3	2	94.1 ± 4.4
Spray Tower	2	1	99.4 ± 0.6
Total	26	12	96.4 ± 2.2

[a] The data from the two-tray absorbers at Site #10 in Table 2.1-8 were excluded from the data set.

reason for deleting the data for the two-tray absorber is that most tray absorbers have three trays, and three-tray absorbers are known to have higher SO_2 removal efficiencies than two-tray absorbers. The average outlet SO_2 emissions per site for all sites was 0.06 lb $SO_2/10^6$ Btu with a standard deviation of 0.062 lb $SO_2/10^6$ Btu. For the oil-fired boilers, the average outlet SO_2 emissions was 0.052 lb $SO_2/10^6$ Btu with a standard deviation of 0.053 lb $SO_2/10^6$ Btu.

Table 2.1-8b shows that absorber type (ignoring the two tray absorbers) has only a slight, if any, effect on SO_2 removal efficiency. The average SO_2 removal efficiency for the 26 scrubbers identified in this table was 96.4 percent with a standard deviation of 2.2 percent.

As discussed in Section 2.1.1.2, SO_2 removal efficiency is a strong function of pH. Due to the lack of pH data in Table 2.1-8, this contention can be neither supported nor refuted. In addition, SO_2 removal efficiency does not appear to be a function of fuel sulfur content.

All sodium scrubbing test results reported in Table 2.1-8 except those for Site #1 were from short-term compliance tests. At Site #1, the scrubber treating flue gas from a coal-fired boiler averaged 96.2 percent SO_2 removal efficiency, which is consistent with the scrubbers treating flue gas from oil-fired boilers. The data from Site #1 were collected from 30 days of continuous emission monitoring (CEM). At sites #7 through #11, short-term CEM compliance tests were performed using ultraviolet photometry. These tests were classified by the EPA as an alternative method to measure SO_2. The EPA Method 8 was the test method used at sites #2 through #6 and sites #12 through #18. Both inlet and outlet SO_2 emissions were measured at nine sites, while at the other nine sites, only outlet SO_2 emissions were measured. The inlet SO_2 emissions at the latter nine sites were calculated from the sulfur content in the oil and AP-42 correlations.

2.1.2 Dual Alkali

The dual (or double) alkali process is the second most prevalent wet FGD technology being applied to industrial boilers today. Since 1974, 13 regeneration systems servicing 27 sodium scrubbers have been installed on industrial boilers. Five regeneration systems have been installed since 1980 to service nine scrubbers. It should be noted, however, that four of the dual alkali systems are known to be currently inoperative.

Of all the industrial wet FGD systems in operation today, approximately one percent are dual alkali systems. Moreover, the use of dual alkali systems has not increased in recent years. The reasons for the lack of current interest relative to the interest in sodium systems are discussed in Section 2.1.2.3. Although dual alkali units comprise a small fraction of the number of wet FGD systems, they account for almost 16 percent of the total SO_2 currently being treated by wet FGD systems. This is because the average boiler size equivalent (BSE) and fuel sulfur content for operating dual alkali systems are both much higher than those for sodium scrubbing systems.

Dual alkali systems are characterized by slightly lower SO_2 removal efficiencies and slightly lower reliabilities than those achieved by sodium scrubbing systems. Based on data from EPA approved tests, the average SO_2 removal efficiency for dual alkali units has been about 90 percent. The reported reliabilities of dual alkali FGD systems range from 80 to 99 percent.

The lime dual alkali (LDA) process is a relatively mature technology. One vendor, however, is currently developing a way to reduce the capital cost for surge capabilities. Surge capabilities are necessary to accommodate the widely fluctuating loads which are characteristic of industrial boiler operation. Furthermore, this vendor predicts that in the near future, dual alkali regeneration plants will be constructed in areas of high sodium scrubber density such as Kern County and New Jersey. These plants will treat the blowdown from sodium scrubbers already operating in these areas and regenerate the sodium reagent for reuse. In addition, methods for substituting limestone for lime in the regeneration section are being investigated. Currently, the cost for raw limestone is about one tenth of the cost for lime. This cost differential provides a considerable incentive for reagent substitution if the technical and economic feasibility of this change can be demonstrated.

2.1.2.1 Process Description. The dual alkali process and chemistry are described in detail in Section 4.2.2.1.1 of the BID. However, there are additions and corrections that deserve mention and are listed below according to the process area.

Absorption

- The absorption process is almost identical to that of sodium scrubbing systems, except for elevated concentrations of trace substances (notably Cl^- and Ca^{+2}) which are the result of closed loop operation.[1,3,28]

Regeneration

- The washwater is not returned to the scrubber directly but rather via the thickener.[31,45]
- All dual alkali processes currently operating in the U.S. use lime as the regenerating alkali. One vendor, however, has recently announced plans to offer a limestone dual alkali process and will begin a pilot operation in 1984.[17] The relative merits of this process are discussed in Section 2.1.2.4.

Solids Separation

- The regeneration reactor effluent, which contains a 1.0 to 1.5 percent suspension of calcium sulfite and sulfate solids as well as soluble sodium sulfite and sulfate, is sent to the solids separation section where the solids are concentrated via a thickener and vacuum filter to approximately 50 percent solids. In most systems, the filter cake is washed with make-up water to reduce the soluble sodium salts in the adherent liquor prior to disposal.[31,45]
- The filter cake can be disposed of directly, stabilized with fly ash, and/or fixated with lime. Fly ash reduces the filter cake's moisture content, thereby improving its stability. By adding lime to the fly ash mixture, a long-term cement-forming process known as pozzolanic action begins. Pozzolanic action is similar to cement curing in that chemical bonds between the lime and the alumina and silica-containing components of fly ash are formed.

The mixture strength increases over a period of several months.[45]

2.1.2.2 Factors Affecting Performance

Since the dual alkali system uses a sodium scrubber, many of the factors affecting sodium scrubbing performance as described in Section 2.1.1.2 are also applicable to the scrubbing section of the dual alkali process. However, there are some important differences. Dual alkali systems generally operate in a very concentrated mode. Whereas the TDS concentrations for sodium scrubbers are typically 5-10 weight percent, those for dual alkali systems are 15-20 percent.[3,46,47,48] The benefits of high TDS concentrations have already been discussed in Section 2.1.1.2. Those reasons that pertain especially to the more concentrated dual alkali systems are discussed in more depth as follows:

- At high TDS concentrations, oxidation is minimized by maintaining a relatively high, steady state sodium sulfate concentration throughout the system.[46,49,50] This inhibits further sulfate formation. Sulfate ions are much more difficult to precipitate out of solution than sulfite ions. The sulfate ion will instead leave the process with sodium. Therefore, high TDS levels in the dual alkali system reduce sodium consumption by reducing sulfate formation.
- Since dual alkali systems are operated essentially in a closed loop mode, it is important that liquid recirculation rates be minimized to minimize the size of vessels and tanks as well as pumping and filtering requirements. These variables are minimized as the TDS concentration increases.
- The higher TDS concentration provides a stronger buffer solution. The control of pH within the narrow range of 6.2-6.8 is essential in dual alkali systems because of corrosion at low pH's and scaling at high pH's. Because of the closed operating mode, chloride accumulates to very high concentrations thus increasing corrosion potential at pH's below 6.0.[3,31] In addition, since

some calcium ions from the regeneration section are carried over to the scrubbing section, there is a great potential for rapid and substantial plugging via calcium scaling above a pH of 7.

- This same buffering capacity leads to stable outlet SO_2 concentrations, even with fluctuations in load and inlet SO_2 concentration. However, with high concentrations of $NaHSO_3$ the SO_2 absorption reaction, $Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$, is equilibrium constrained.

The other factors affecting scrubber performance such as liquid-to-gas ratio and absorber design are the same as those discussed in the sodium scrubbing section. These will not be repeated here; instead, the reader is referred to Section 2.1.1.2.

The predominant factors affecting regeneration are the sulfur and chloride contents of the fuel. The combustion of low sulfur coal results in a higher ratio of oxygen to sulfur dioxide in the flue gas than does the combustion of high sulfur coal. A higher relative oxygen content promotes the oxidation of a higher percentage of sodium sulfite to sodium sulfate. This can cause two major problems: (1) a lower liquid phase alkalinity due to higher $SO_4^=$ and lower $SO_3^=$ levels in solution and thus a lower SO_2 removal capability; and (2) potentially higher sodium losses due to the requirement for a Na_2SO_4 purge stream.

Dual alkali systems operate in a relatively closed-loop mode, except for the water evaporated in the scrubber and that which is occluded in the waste sludge. Because of this, substances that exist only in trace amounts in sodium scrubbing systems can build up to high steady state concentrations in the dual alkali process. Chloride, which is volatilized from the coal in the boiler and absorbed in the scrubber, is the most corrosive of the substances contained in coal. In some cases, chloride can reach concentrations of up to 40,000 ppm in the scrubbing liquor.[3]

High chloride concentrations lead to high sodium losses and contribute to stress corrosion. Sodium losses increase because sodium, a positive ion, will pair with chloride, a negative ion, to insure charge conservation in the scrubbing liquor. This effectively ties up the sodium that would otherwise be associated with an alkaline ion such as $SO_3^=$. Since chlorides are removed in soluble form (either as a liquid purge or as occluded liquor in the solid waste), a corresponding amount of sodium will be lost along with any chloride purged from the system. High chloride concentrations at pH's below 6.2 can substantially and rapidly corrode all sections of a dual alkali system.[3]

One proposed solution to the chloride problem is to use a prescrubber to remove chlorides before the flue gas enters the dual alkali system. However, the use of a prescrubber with a separate liquor loop will cause water balance problems in the system. Since all the evaporation loss would occur in the prescrubber, the only water loss from the double alkali system would be the water included with the sludge. The make-up water rate for this small water loss would not be sufficient to meet requirements for normal cake washing (more than one displacement wash), demister washing, pump seals, and lime slaking.[51] Another source agrees that prescrubbers are not a viable solution to the chloride problem. This source contends that the installation of Inconel or Hastelloy G alloys is the only feasible deterrent to corrosion.[3]

2.1.2.3 Applicability to industrial boilers

Table 2.1-9 presents a summary of double alkali scrubbing systems, both currently operative and inoperative, that have been installed on domestic industrial boilers. It presents such pertinent information as operating status, boiler size equivalent, number of scrubbers per unit, and fuel type and sulfur content. Thirteen dual alkali systems have been installed since the early 1970's. All of these plants except one have only one dual alkali system; the exception has two complete dual alkali systems. The 13 regeneration sections service a total of 27 scrubbers and an average of 520 x 10^6 Btu/hr BSE (the average BSE for the scrubbers is 230 x 10^6 Btu/hr). The average fuel sulfur content is 2.81 weight percent. The dual alkali systems that are currently operating represent about one percent of the total industrial wet FGD systems operating today and they treat about 16 percent of the total SO_2 treated by industrial boiler wet FGD systems.[5]

TABLE 2.1-9. APPLICABILITY OF DUAL ALKALI SYSTEMS INSTALLED ON INDUSTRIAL BOILERS

Company/Location	Vendor	Start-up Date	Operating Status	Boiler Size Equivalent (10^6 Btu/hr)[a]	No. of FGD Units	No of Scrubbers[b]	Fuel Type[c]	Fuel %S	Absorber Type[d]
Caterpillar Tractor Co.[52,53] East Peoria, IL	FMC	1978	Operative	940	1	4	C	3.2	VS
Joliet, IL	Zurn	1974	Operative	300	1	2	C	3.2	TA
Mapleton, IL	FMC	1974	Operative	1060	1	2	C	3.2	VS
Morton, IL	Zurn	1978	Operative	170	1	2	C	3.2	TA
Mossville, IL	Zurn	1975	NA	630	1	4	C	3.2	VS
Firestone[53,54] (now Occidental) Pottstown, PA	FMC	1975	Shut-down (Company change)	36	1	1	C	2.5-3.6	VS
General Motors[55] Parma, OH	GM	1974	Operative	570	1	2	C	2.5	TA
Santa Fe Energy Corp[56,57] Bakersfield, CA	FMC	1979	Operative	310	1	1	O	1.5	DD
ARCO Polymers[31] Monaca, PA	FMC	1980	Operative	1360	1	3	C	3.0	DD
Grissom Air Force Base[58] Peru, IN	Neptune/ Airpol	1981	Operative	140	1	2	C	3.0-3.5	VS
St. Regis Paper[59] Sartell, MN	Neptune/ Airpol	1983	Inoperative (Plugging)	590	1	2	C	1.4	PB
Mississippi Army Ammunitions Plant[60] Bay St. Louis, Miss	Zurn	1983	Inoperative (plugging)	150	2	2	C	3.0	PB
Total				6300	13	27			
Average Per Plant				520	1.1	2.3		2.81	

[a] These values represent the BSE for the overall scrubbing system, not for the individual scrubbers.

[b] These values represent the number of scrubbers serviced by the regeneration section(s).

[c] C = Coal; O = Oil.

[d] VS = Venturi Scrubber: TA = Tray Absorber: DD = Disc and Donut Contactor: PB = Packed Bed

Nine of the thirteen regeneration systems are known to be operating at this time; four are known not to be operating (see Table 2.1-9). Of these six, three are inoperative due to plugging, while one is inoperative due to a company takeover.[54,59,60] Two of these systems are operating as sodium scrubbing systems, disposing of their wastewater directly to a local sewerage system.[60] The other unit is removing only particulate matter; the boiler it serves is currently burning a compliance coal to meet state SO_2 regulations.[59]

Since 1980 five systems have been installed, and of these five, only two are operative. The lack of current demand relative to the demand for sodium systems may be explained to a large extent by the following:

- Reliability factors for industrial dual alkali systems are slightly lower than those for sodium scrubbing systems (see Section 2.1.2.5).
- Dual alkali systems are more complex than sodium scrubbing systems and therefore require more operator attention.
- Dual alkali systems are less economical than sodium scrubbing systems, especially for low SO_2 loadings.

2.1.2.4 Development status

Although lime dual alkali is a mature technology, it is undergoing several developments. One source is predicting that, in the near future, centralized dual alkali regeneration plants will be installed in areas of high sodium scrubber density. It claims that there is enough economic incentive now for private contractors to construct plants to regenerate the spent sodium salts of the scrubber blowdown. After the sodium has been exchanged for calcium, it will be sold back to the scrubber operators for reuse in their systems. In most cases, the cost of calcium sludge waste disposal will be lower than the cost of disposing the sodium blowdown stream. Currently, there are bids out to build two regeneration systems: one to service sodium scrubbers operating on 63 steam generators and the other to service sodium scrubbers operating on 20 steam generators.[3]

One vendor is evaluating methods of substituting limestone for lime in the regeneration step. Currently, the cost for raw limestone is about one-sixth the cost of lime. This cost differential provides a considerable incentive for reagent substitution if the technical and economic feasibility of this change can be demonstrated. A limestone dual alkali (LSDA) process was tested in a pilot scale system at Gulf Power Company's Plant Scholz in 1981; another extensive test is planned by EPRI at Northern Indiana Public Service Co. (NIPSCO) for early 1984.[17,47]

At the Scholz plant, the average SO_2 removal efficiency was 95.8 percent. However, this SO_2 removal efficiency might not be typical of LSDA systems since it appears that the unit was operated in the dilute mode. The pH of the effluent from the scrubber was consistently below 6.0, which is not the pH that would have been expected if the system had been operated at the design TDS concentration of 20 weight percent.[61] In other words, the operating TDS level appears to have been much lower than the design TDS level.

Limestone utilizations were high, over 97 percent. However, the waste sludge solids content (at 35 to 45 percent) was well below the design value of 55 percent. In addition, the soda ash consumption of 0.29 moles of Na_2CO_3/mole of SO_2 removed far exceeded the design value of 0.04. These two problems might have been the result of the mechanical performance of the equipment, which, recomissioned after three years of inactivity, was poor.[47] Despite the initial poor performance in these two areas, one vendor claims that sodium consumption should be between about 0.02 to 0.05 moles Na/mole SO_2 removed and that the solids content should be in the range of 50 to 70 percent for LSDA systems.[17]

2.1.2.5 Reliability

Reliability data for industrial boiler and utility boiler dual alkali systems are presented in Table 2.1-10. Included with the table are the capacities of the systems, the period over which the data were collected, and the type of index reported by the plant. Most of the plants kept availability indices; Louisville Gas & Electric reported a reliability value; Caterpillar reported an operability value; and neither Santa Fe Energy nor Occidental Petroleum specified its index of reliability. Behrens

TABLE 2.1-10. RELIABILITIES FOR DUAL ALKALI SYSTEMS

	FGD Systems Capacity (10^6 Btu/hr)	Period of Data Collection	Index Reported	Reliability(%)
Sante Fe Energy Co.[56]	310	48	NA[b]	99
ARCO[31]	1,360	12	Availability	97.6
Firestone Tire & Rubber[54] (now Occidental Petroleum)	40	NA[b]	NA[b]	80
Caterpillar[52]	940	NA[b]	Operability	90
Louisville Gas & Electric[a,62]	2,700	12	Reliability	94.1
Southern Indiana Gas & Electric Co.[a,63]	2,600	13	Availability	96.7
Central Illinois Public Service Co.[a,64]	5,700	9	Availability	96

[a] Utility systems.

[b] NA = Not Available.

reports an average availability for the three utility systems presented in Table 2.1-10 of 96.5 and an average operability of 79.7.[65]

Since the data are for various indices and from both utility and industrial systems, a statistical analysis is not justified. Nevertheless, the consistently high values indicate that dual alkali systems are highly reliable.

2.1.2.6 Emission data

The emissions data for industrial boiler dual alkali systems are presented in Table 2.1-11 in terms of percent SO_2 removal efficiency and outlet SO_2 emissions (lb $SO_2/10^6$ Btu). Data for all six scrubbers were obtained using EPA methods. The General Motors test lasted more than one month; the Grissom Air Force Base and ARCO data were from compliance tests; and the Santa Fe Energy data were from a recent in-house study.[31,56,57,66,67,68] The average SO_2 removal efficiency was reported to be 91.0 percent with a standard deviation of 2.4 percent. The average SO_2 emissions in the scrubber outlet was 0.38 lb $SO_2/10^6$ Btu with a standard deviation of 0.20 lb $SO_2/10^6$ Btu. Actual outlet emissions ranged from 0.091 to 0.65 lb $SO_2/10^6$ Btu, depending on both the fuel sulfur content and the actual SO_2 removal efficiency.

Two other tests not listed in the table deserve mention. They are the long-term testing at Gulf Power Company's Plant Scholz pilot operation and the recent year long test at Louisville Gas and Electric's Cane Run 6 system. Average SO_2 removal efficiencies for these two tests were 95.5 and 92.0 percent, respectively.[50,62]

Theoretically, any wet FGD system can achieve very high (99+ percent) SO_2 removal efficiencies. This applies even to systems that use no alkaline reagent and scrub with water only - however, only if very high L/G's are used. Likewise, dual alkali systems can theoretically achieve very high SO_2 removal efficiencies. However, under normal operating conditions, they have shown that they can achieve only around 90 percent. This is because most are operated with high TDS concentrations (15 - 20 percent), which as was discussed in Section 2.1.1.2, increase the equilibrium partial pressure of

TABLE 2.1-11. EMISSIONS DATA FOR DUAL ALKALI SYSTEMS USING EPA TESTING METHODS

Company/Location		Fuel Type	Sulfur Content of Fuel (wt.%)	Outlet Emissions (lbs $SO_2/10^6$ Btu)	SO_2 Removal Efficiency (%)
ARCO Polymers[31] Monaca, PA		Coal	2.5 - 2.8	0.65	88
General Motors[67] Parma,OH	Scrubber I	Coal	2.5	0.30	92.2
	Scrubber II	Coal	2.5	0.32	91.6
Grissom Air[68] Force Base Peru, IN	System I	Coal	3.0 - 3.5	0.56	88.1
	System II	Coal	3.0 - 3.5	0.38	94.2
Santa Fe Energy[56,57] Bakersfield, CA		Oil	1.5	0.091	91.7
Average			2.61	0.38	91.0

SO_2. When dual alkali tests have been operated in the dilute mode, they have shown removal efficiencies similar to those achieved by sodium scrubbing systems. For example, testing at Plant Scholz of both the LDA and LSDA processes provided SO_2 removal efficiencies of 95.5 and 95.8 percent, respectively.[50] Although not stated specifically, the absorbers effluent pH indicated that both systems were operated in the dilute mode. Therefore, the relatively low efficiencies reported by commercial-scale industrial systems, which typically operate in the concentrated mode, appear to be consistent with theory.

2.1.3 Limestone Wet Scrubbing

Limestone wet scrubbing has been applied at only one industrial boiler site and its industrial sector demand appears limited within the near future for the following reasons:

- Compared to clear liquor (sodium or dual alkali) scrubbers, limestone systems require considerably more operator attention and skill, due to the potential for scaling. Scaling is a result of the relative insolubility of limestone (calcium carbonate) in water, being 1/14,000 as soluble as sodium carbonate. Since industrial applications are less likely to have sophisticated instrumentation, a pool of skilled operators and technicians, or spare scrubber modules than their utility counterparts, scaling and lower scrubber reliabilities are likely.
- The high initial capital costs of limestone scrubbing favor sodium-based scrubbers for the smaller boiler sizes encountered in industrial applications.
- Due to the potential for scaling in limestone systems, it may be more difficult to achieve high sustained SO_2 removal efficiencies in limestone scrubbers compared to more soluble lime and sodium-based scrubbers.

In general, unbuffered calcium-based absorption (limestone/lime) achieves lower sustained SO_2 removal efficiencies than sodium-based absorption on comparable applications. As an illustration, the two limestone demonstrations at the Springfield Utilities Southwest Station and

Rickenbacker Air National Guard Base (RANGB) both measured unbuffered, limestone system removal of SO_2 on high sulfur coal application of 50 to 70 percent. As shown by sections 2.1.1.6 and 2.1.2.6, typical removal efficiencies on high sulfur coal controlled by sodium and dual alkali scrubbers have ranged from 85 to 99 percent. Mass transfer additives such as adipic acid and dibasic acid can significantly increase SO_2 removal efficiencies for limestone systems. SO_2 removal efficiencies of 90 to 96 percent have been achieved at several utility sites, while a 30-day average of 94.3 percent SO_2 removal was achieved at one industrial site.

Because of the limited number of limestone industrial applications, and the unique design features of that one application, the performance of limestone scrubbing in industry can only be estimated based on utility experience. Behrens reports that limestone FGD availability in the utility industry is the lowest of all absorbents, averaging 73.5 percent.[65] This does not compare favorably with lime at 84.1 percent and dual alkali at 96.2 percent.[65] While other studies have shown how limestone FGD reliabilities can be significantly improved through improved instrumentation, maintenance and operating practices, and spare modules, the perception remains that where minimal operator attention and expertise is applied, the most reliable FGD systems, and the overwhelming choice of industry, are, and will continue to be, sodium-based systems.

One noteworthy statistic that has not been discussed previously is the effect of SO_2 loading on FGD reliability. Since the Behrens data above include a disproportiate number of medium and high sulfur coal applications, limestone FGD reliabilities on low sulfur coal applications tend to be much higher than those values previously cited. For example, one limestone FGD system tested by the EPA in 1979, which achieved better than 95 percent SO_2 removal for a 30-day period on a 0.55 percent sulfur coal, has achieved, along with a sister unit, essentially 100 percent reliabilities in recent years. Therefore, on low sulfur coal applications in industrial boilers, limestone FGD may be a reasonable alternative.

2.1.3.1. Process description. The process chemistry, equipment, and operations for this system are described in the March 1982 BID. However, a more detailed process flow diagram is included in Figure 2.1-3 to replace the simplified diagram in the BID.[69]

2.1.3.2 Factors affecting performance. Limestone wet FGD systems are confronted with two major chemical-related problems affecting their performance. These are the relative insolubility of the reagent and the susceptibility of the systems to scaling or plugging. These two problems are the major considerations in the design and operation of limestone systems. They affect the following variables:

- Reagent requirements
- Liquid-to-gas ratio (L/G)
- Usage of soluble species and additives
- Slurry pH
- Reaction tank residence time
- Scrubber design
- Reaction tank configuration

The SO_2 removal performance of sodium or dual alkali FGD systems is limited only by gas-liquid mass transfer in the scrubbing step since all of the alkalinity required for reaction with SO_2 is available in soluble form. Calcium-based systems, on the other hand, rely on solids dissolution to provide most of the alkalinity required for SO_2 absorption. Since liquid-solid mass transfer tends to be significantly slower than gas-liquid mass transfer, lime and limestone systems must be operated differently than the other two wet FGD system, as described below.

Reagent requirements Unlike sodium scrubbers which operate at an Na_2CO_3/SO_2 stoichiometric equivalent ratio of less than one, limestone systems operate at higher ratios because of limestone's relatively slow dissolution rate. In other words, reagent utilization for limestone systems is generally much lower than that for sodium-based systems. Although it is generally agreed that SO_2 removal is a function of the amount of excess

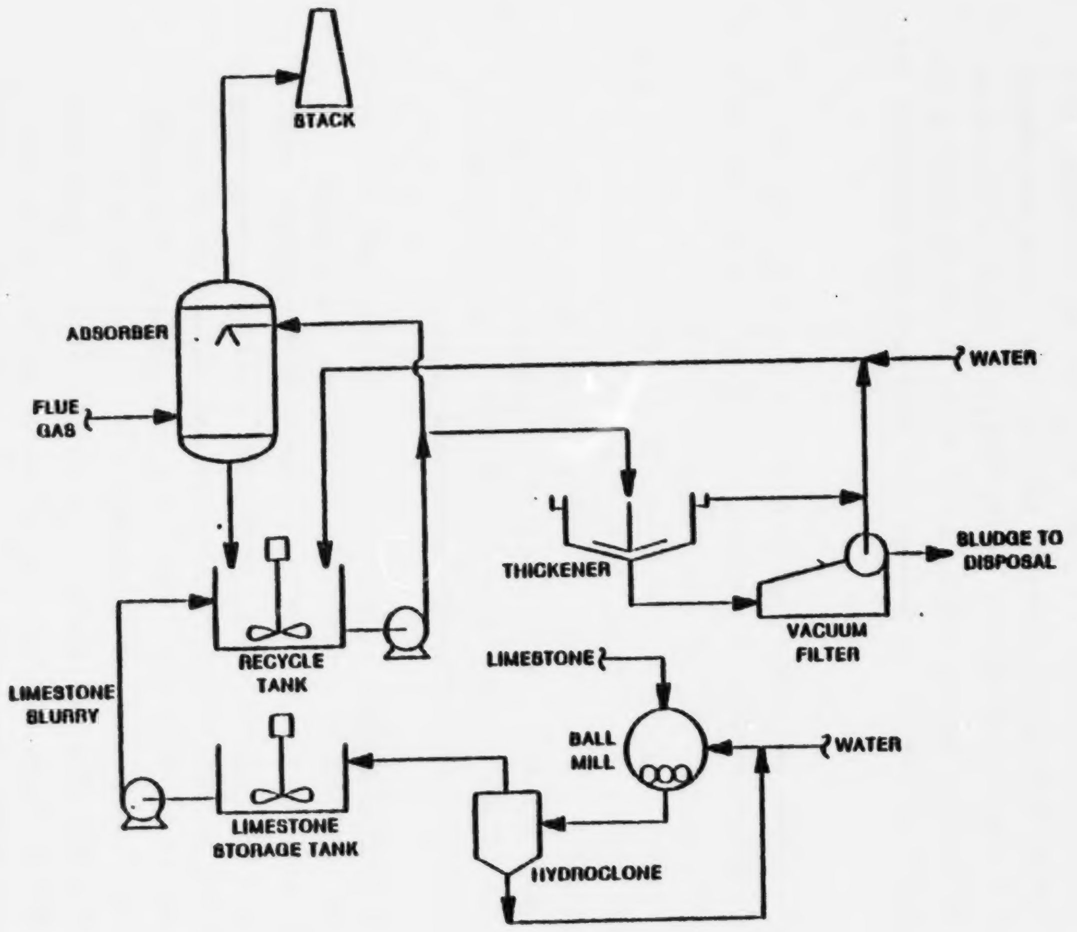


FIGURE 2.1-3. LIMESTONE PROCESS FLOW DIAGRAM

limestone in solution, there is not a consensus concerning the levels required. For instance, data from TVA's Shawnee Power Station in Paducah, Kentucky show that SO_2 removal increases rapidly with increasing limestone stoichiometry up to approximately 1.4 moles $CaCO_3$/mole SO_2 absorbed. Data collected by Radian Corporation, however, indicate that little improvement in SO_2 removal is realized by increasing the limestone stoichiometry above 1.1.[70]. The differences between these results might be attributable to the different sources of limestone and the specific hold tank configurations for each system.

L/G Ratio - Higher SO_2 removal efficiencies are achieved, and the chances of scaling are reduced, at higher L/G ratios up to the point where flooding and poor gas distribution occur. Typical L/G's for all calcium-based systems range from 9 to 15 ℓ/m^3 (60 to 120 gal/1,000 ft^3) with the higher number being more typical for high sulfur coals.[17,71] For comparison, typical L/G's for sodium scrubbing systems range from 0.7 to 7.8 ℓ/m^3 (5 to 50 gal/1,000 ft^3). As a result of the greater liquid flow, pumping requirements and thus electricity costs will be several times greater for limestone systems than for sodium-based systems.

Effects of Soluble Species - The concentration of dissolved ions other than Ca^{+2} in the scrubbing slurry directly affects the liquid phase alkalinity and hence the system's ability to remove sulfur species from boiler flue gas. The important ions are Na^+, Mg^{++}, and Cl^-. These soluble ions can enter the system as Na_2O or MgO in the ash, $MgCO_3$ from Thiosorbic limestone, or HCl in the flue gas. They can also be added to the system with an additive.[70] Magnesium and sodium assist in SO_2 scrubbing by maintaining additional alkaline species in solution. This improvement in SO_2 scrubbing due to increased magnesium and sodium concentrations in scrubbing liquors is well documented.[72,73,74,75] On the other hand, high chloride levels are generally thought to be detrimental to SO_2 removal since chloride ions tie up the alkaline species and result in excessive alkalinity losses. Some organic acids, such as adipic acid and dibasic acid, have been used to enhance limestone dissolution and SO_2 removal. Their effect is much the same as an increase in alkalinity due to Mg^{+2} and Na^+ addition.[70]

Slurry pH - The operating pH selected for calcium-based systems involves a tradeoff between reagent utilization and SO_2 removal efficiency. The more acidic the slurry is the greater the reagent utilization will be; whereas the more alkaline the slurry is the greater the SO_2 efficiency will be. For all calcium-based systems, operating at too high a pH can cause scaling. For limestone systems, the optimum slurry pH is between 5 and 6.[76]

Reaction Tank Residence Time - Residence time in the reaction or hold tank is determined by the size of the reaction tank and the liquid flow rate. It is an especially important parameter in limestone systems because of limestone's relatively slow dissolution rate. Larger reaction tank residence times lead to greater limestone dissolution and hence higher limestone utilization. However, the actual residence times used will be a tradeoff between the costs associated with the reaction tank, pumping requirements, and reagent costs. Besides reducing limestone utilization, large hold tanks can reduce operating costs by producing large, easy to dewater crystals.[70]

Another important factor affecting limestone utilization is particle size. The smaller the limestone particle is the greater the surface/volume ratio and thus the greater the limestone dissolution rate will be. However, too small a size can actually render the particle ineffective because water effectively "blinds" the particle by shielding it from other water molecules. As a result, the limestone does not dissolve as well.[49]

Scrubber Design - Because packed bed scrubbers are very efficient gas absorption devices, they were used in the original lime and limestone wet FGD systems. However, due to problems with plugging in packed beds, the trend, over the last several years has been away from packed beds to open spray towers, which are more reliable and easier to maintain.[77]

Gas maldistribution can be a major problem in limestone spray absorbers, particularly in large units. Portions of the scrubber can become liquid phase alkalinity-limited due to gas maldistribution, even though the total alkalinity entering the scrubber is sufficient for good SO_2 removal. Some scrubber designs, therefore, incorporate straightening vanes and/or open packing to promote good gas distribution.[76]

Reaction Tank Configuration - Reaction tank configuration also has been shown to have an effect on both limestone utilization and SO_2 removal. One source indicates that plug flow reaction tank designs can yield significant improvements in limestone utilization and SO_2 removal. (A plug flow design is one that allows the reacting stream to flow through the reactor such that there is no backmixing. A plug flow situation can be approximated by a number of mix tanks in series.) For a constant limestone addition rate, the SO_2 removal efficiency at TVA's Shawnee Station increased from 70 to 79 percent by changing the reaction tank from a single stirred tank to three identically-sized tanks in series. This plug flow effect apparently drives the limestone dissolution reaction further toward completion and makes more liquid phase alkalinity available for reaction with absorbed SO_2.[70]

Solid Waste Disposal - An important operational area which is associated with all calcium-based flue gas desulfurization (FGD) systems is the dewatering and disposal of the solid phase reaction products. Conventional limestone systems produce a sludge composed primarily of calcium sulfite which, because of its crystalline properties, may require special handling. This sludge is thixotropic: that is, it reliquefies upon application of stress and does not dewater well. Consequently, ponding is the normal method of ultimate disposal. However, further problems can arise with ponding due to process liquor infiltration of ground water. Plastic or clay liners are usually required to prevent this type of contamination. Currently, FGD wastes are classified as non-hazardous according to RCRA regulations, pending the outcome of an EPA study examining these wastes. A recent innovation, forced oxidation, is being employed at many new systems to oxidize calcium sulfite to calcium sulfate, thereby improving the dewatering and handling properties of the sludge.[78] Many commercial processes also fixate the sludge by adding dry lime or limestone.

2.1.3.3 Applicability to industrial boilers. Currently the only limestone wet FGD system operating on an industrial boiler is located at the Rickenbacker Air National Guard Base (RANGB) (see Table 2.1-12). Since the boiler is used only to provide space heating, it is used only six months out of the year.[80] No other calcium-based wet FGD system for an industrial boiler application has been reported to have used or to be using limestone. Furthermore, the major suppliers of utility limestone FGD systems predict that few, if any, new industrial boiler limestone systems will be installed in the near future.[81,82,83]

It should be noted, on the other hand, that the limestone wet FGD process is a proven technology in the utility industry. As of November 1982, limestone systems represented over 50 percent of the 190 utility FGD systems that had been installed and about 56 percent of the total scrubbing capacity (both wet and dry).[84] This discrepancy in limestone wet scrubbing usage between industry and electric utilities is primarily due to the perception that limestone systems are less reliable than sodium-based systems. Also, despite the recent developments in the use of mass transfer additives, forced oxidation, and spray tower designs, limestone systems still have higher capital and annualized costs than sodium-based systems, especially for small BSE's. The capital costs are much higher for limestone systems because there are more equipment items, and the similar equipment items (such as the scrubber) are larger to compensate for the relative insolubility of limestone. Also, it is much more expensive to maintain high reliabilities for limestone systems than it is for sodium scrubbing systems. For example, studies have shown that more sophisticated instrumentation, greater maintenance costs and operator attention, as well as spare absorbers are required for a limestone wet FGD system to have consistently high reliabilities.[85] Despite these additional costs, limestone FGD systems are economically attractive for utility boilers because the cost differences

TABLE 2.1-12 SUMMARY OF LIMESTONE SYSTEMS OPERATING ON U.S. INDUSTRIAL BOILERS AS OCTOBER 1983

Process	Vendor	Company/Location	Start-up Date	Number of FGD Units	Size (acfm)	Fuel	
						Type	Sulfur(%)
Lime	Research	Rickenbacker Air National Guard Base Columbus, OH[79]	3/76	1	55,000	Coal	3.6

between soda ash and limestone exceed the additional capital and maintenance costs. However, even for large industrial applications where limestone systems appear to enjoy an annual cost advantage, boiler owners seem to be reluctant to apply the technology because of the large capital investment required.[3]

2.1.3.4 Development status - Limestone wet scrubbing technology is well established and widely applied in the utility industry. Currently, there are several efforts focused on ways to improve performance, cost effectiveness, reliability, and waste disposal for limestone systems. The recent innovations worth mentioning are: the use of mass transfer additives, forced oxidation, and advanced absorber designs.

Mass Transfer Additives - Both inorganic and organic additives have been used to improve the SO_2 removal efficiency and reagent utilization of limestone systems. These additives are used because of the limestone's low solubility in water. This low solubility results in a low liquid phase alkalinity, making it necessary to contact the acidic flue gas with large slurry volumes. The liquid to gas ratio (L/G) for limestone systems is typically 60 to 120 gallons per thousand cubic feet of gas, depending on the SO_2 concentration and the desired removal level. Recirculating this large amount of slurry consumes a large portion of the system's electrical power. Maintenance on these large pumps is often difficult and time consuming due to their size.[71]

Several additives are being used commercially which increase the liquid phase alkalinity of limestone systems. Magnesium oxide is currently the most widely used additive. However, since chlorides effectively tie up the magnesium, the application of MgO will be limited to open loop systems. In closed loop systems, chlorides (originally present in the feed coal) are concentrated in the recirculating slurry to high levels. Prescrubbers for chloride control can mitigate this problem, but create other operating problems such as wastewater disposal, water balance impacts, and chloride stress corrosion.[3] For these reasons, prescrubbers are not commonly employed for chloride control. Adipic acid and waste dicarboxylic acids obtained during the production of adipic acid are also being used in utility installations. Since these acids do not react with chlorides, their ability to enhance SO_2 removal is not affected by the high chloride concentrations that are sometimes encountered in closed loop operations.[71]

Adipic acid is a commercially available dicarboxylic organic acid in powder form, used primarily as a raw material in the nylon-manufacturing industry and with some applications as a food additive. The capability of carboxylic acids to improve SO_2 removal and limestone utilization has been known for over 10 years. Most of the initial research in this area was performed by Dr. G. T. Rochelle of TVA. More recently, EPA has sponsored adipic acid testing at its RTP laboratory facility, the Shawnee Prototype unit, a full-scale utility in Springfield, MO, and the Rickenbacker Air National Guard Base (RANGB) near Columbus, Ohio.[71] Dibasic acid (DBA) is a by-product of adipic acid and costs about half as much. It is a mixture of adipic, succinic, and glutaric acids. It has been shown to have the same effects as adipic acid and is currently preferred because of its lower cost.[71]

DBA effectively buffers the pH in limestone absorbers and improves the SO_2 removal efficiency. This buffering action limits the drop in pH at the gas/liquid interface during absorption. The resulting higher concentration of SO_2 at the interface accelerates the liquid-phase mass transfer. Thus, SO_2 absorption becomes less dependent on the limestone dissolution rate to provide the necessary alkalinity. This makes it possible to achieve a higher SO_2 removal efficiency at a lower L/G and limestone stoichiometry. The optimum concentration range of DBA for effective SO_2 removal is at 700 to 1500 ppm with a pH greater than 5.2 at the scrubber inlet.[86] However, there are difficulties with increased degradation of DBA when pH's greater than 5 at the scrubber inlet are used. These impacts, though unfavorable, are not seen to be a serious threat to the process.[86] Preliminary economic evaluations have shown that DBA can reduce both the capital investment and the operating costs of limestone systems while simultaneously improving the performance, even where the actual addition rate of DBA is three to five times the theoretical requirement due to the degradation of the acid.[87] One study shows a decrease of about 10 percent in total levelized costs for a 500 MW system firing a high sulfur coal even at high degradation levels.[88]

Studies indicate a substantially greater limestone utilization when either adipic acid or DBA is used. The Shawnee test showed that at pH levels lower than 5.2, the limestone utilization is usually greater than 85 percent for an adipic acid-enhanced limestone system, as compared to 65 to 70 percent utilization at the higher pH needed in unbuffered limestone systems to achieve an equivalent SO_2 removal. Thus, an adipic acid- or DBA-enhanced system consumes less limestone, generates less waste sludge, and reduces cost. In addition, high limestone utilizations contribute to more reliable scrubber operation.[89]

Forced Oxidation - Forced oxidation is a process modification in which air is sparged into a reaction tank - usually the recycle tank - to oxidize calcium sulfite ions to calcium sulfate ions. This improves system operation by preventing scaling and by making the FGD sludge easier to handle and dispose.[71]

During the operation of first generation lime and limestone FGD systems, calcium sulfate scaling on system internals was often a serious problem. Oxygen from the flue gas reacted with sulfite ions and formed sulfate ions. This "natural" oxidation is generally between 10 and 30 percent of the total SO_2 removed. It has been found that for oxidation of less than 15 percent, calcium sulfate scaling does not occur. This is due to a coprecipitation mechanism in which sulfate ions are interspersed throughout the crystal lattice replacing sulfite ions. This coprecipitation mechanism can keep the scrubbing solution subsaturated with respect to calcium sulfate. At oxidation levels above 15 percent, the coprecipitation mechanism is not capable of removing all of the sulfate ions from the solution. Since very few calcium sulfate, or gypsum ($CaSO_4$ - $2H_2O$), seed crystals are present, crystal growth (scaling) on the system internals may occur to reduce the relative saturation.[71]

One possible solution is to control the process such that the oxidation fraction is less than 15 percent. However, since oxidation is a function not only of flue gas oxygen levels but also of SO_2 concentrations, contactor design, and other liquid and gas phase parameters, it is difficult to control this simply by maintaining low excess air levels. An alternative to operating with low oxidation fractions is, paradoxically, to operate at the other end of the spectrum -- with high oxidation fractions. This provides sufficient gypsum seed crystals in solution to prevent crystal growth on scrubber and pipe surfaces. Additionally, sludge handling characteristics with forced oxidation are greatly improved over unoxidized solids due to the high concentration of gypsum. Gypsum is a structurally stable solid which can be stacked to heights of over 100 feet for temporary and permanent disposal.[71]

In most forced oxidized systems, air is sparged into the reaction tank at a stoichiometry of 2 to 4 moles of oxygen per mole of SO_2 removed. Other methods of oxidation have been examined by TVA at the Shawnee pilot scrubbers. At least one commercial vendor uses a double loop system to produce gypsum. The second liquor loop, at a higher pH, is used to remove the bulk of the SO_2 via oxidation. Excess liquor is passed to the front where the pH drops and most of the oxidation takes place. This design also promotes good limestone utilization.[71]

Absorber Design - As discussed previously, the major trend in absorber design has been away from packed contactors and towards open spray towers. This is due to the relatively high reliability and easy maintenance of open vessels. The classical spray tower, which uses small high-energy nozzles and relatively low gas velocities, is not practical for limestone FGD systems. However, spray towers with high L/G's developed for these applications have been shown to exhibit exceptionally outstanding performance. Very high SO_2 removal efficiencies (95 percent) have been achieved with reliabilities approaching 100 percent.[77] There is one major problem with spray tower operation, however, and that is the mist eliminator. In this part of the system, gas flow is restricted and the potential for plugging and scaling is increased. To reduce the severity of this problem, various washing schemes have been developed.[77]

Two new absorber designs have recently been evaluated which offer alternatives to the more conventional counter current design: the cocurrent absorber, such as that recently evaluated by EPRI and TVA, and the jet bubbling reactor used in the Chiyoda CT-121 process.[71]

2.1.3.5 Reliability. Reliability data for industrial limestone FGD systems are scarce since only one system is currently operating. Scrubber performance at the RANGB facility has generally been quite good except for the early stages of operation during which several start up problems caused significant amounts of downtime. From November 1976 through December 1978, the RANGB system demonstrated that an industrial boiler limestone FGD system can operate with high reliability. During this period, it operated about 95 percent of the the time, excluding the downtime caused by a severe blizzard.[90] It should be noted that part of its high reliability might have been attributable to the fact that it operates only 6 months out of the year and thus would provide more time for maintenance and repair than is typical for other systems.[80] Also, the unique design of RANGB's FGD system gives it a more steady operation with a constant liquid-to-gas ratio. However, this steady operation is achieved at the expense of higher electricity, solid waste disposal, and reagent costs.[90]

In a recent study performed for the EPA, 24 utility-size limestone systems were evaluated. These systems had an average availability of only 73.5 percent and an average operability of 73.8 percent. The primary components of failure and the percentage of system outages resulting from these failures were: dampers (28 percent), duct systems (19 percent), fans (17 percent), absorber towers (16 percent), and mist eliminators (9 percent).[65] While this study affirms that reliabilities are in general relatively low, one EPA test conducted in 1979 showed that reliabilities for systems in which low sulfur coal is used can achieve exceptionally high reliabilities. For example, one limestone FGD system which achieved better than 95 percent reliability for a 30-day period on a 0.55 percent sulfur coal has achieved, along with its sister unit, essentially 100 percent reliabilities over the last several years.[91,92]

Although many improvements in design and operation have been identified to improve limestone systems, the conclusion reached by industrial clients is that additional effort has to be expended in order to make limestone systems acceptable where reliable steam supply is paramount. The implication is that the extra risk/effort associated with limestone FGD is offset by economic advantages on utility applications, but this economic advantage is not present for industrial size applications. It is therefore not surprising that the vast majority of industrial FGD systems are sodium-based and not calcium-based.

2.1.3.6 Emissions data. Emissions data for limestone and limestone-adipic acid systems for the industrial unit at RANGB are reported in Section 4.2.5 of the BID. These data are from a 30-day test on a boiler firing 3.5 percent sulfur coal. To summarize this section, 50-70 percent SO_2 removal efficiency was achieved with limestone alone, and 94.3 percent was achieved when adipic acid was used. Actual long term emission data at Springfield Utilities in Missouri confirm RANGB's test results.[93] Without a mass transfer additive the SO_2 removal efficiencies at that facility were 50-70 percent. With a mass transfer additive, target SO_2 removal efficiencies of 80, 90 and 95 percent were achieved over periods ranging from 7 to 30 days.[94] One 31-day test at the TVA Shawnee Plant with adipic acid gave an average of 96.1 percent SO_2 removal efficiency.[93]

2.1.4 Lime Wet Scrubbing

Although lime is about 100 times more soluble in water than limestone, it still presents the same chemical problems that are inherent to all calcium-based systems. Like limestone systems, there is only one lime system currently operating in the industrial boiler market, and this system has unique cost advantages.[95] The plant at which this scrubber is located uses the lime slurry blowdown to neutralize and precipitate metal ions out of wastewater streams generated by other processes within the plant.

According to the vendors of utility wet lime systems, it is unlikely that very many, if any, new systems will be installed on industrial boilers over the next five years.[81,82,83] This lack of demand in the industrial sector is primarily because lime systems are affected by the same problems that affect limestone systems as discussed in Section 2.1.3.

The owner of the only currently operating industrial lime system, Pfizer, Inc., reports achievements of greater than 90 percent SO_2 removal efficiency and 95 percent reliability. SO_2 removal efficiencies and reliabilities for utility lime systems have typically been much lower for comparable high-sulfur coal applications.

2.1.4.1 Process description. The process, chemistry, equipment, and operations for this system are described in the March 1982 BID and will therefore not be repeated here.

2.1.4.2. Factors affecting performance. Like limestone systems, lime wet FGD systems are confronted with two major chemical-related problems affecting their performance. These are the relative insolubility of the reagent and the susceptibility of these systems to scaling or plugging. These two problems are the major determinants in the design and operation of lime and limestone systems.

Because they have similar chemistry, lime and limestone systems operate similarly. For example, the L/G ratios are about the same (although L/G's for lime systems are slightly less), and new lime scrubbers tend to be open vessels rather than packed or tray towers.

However, since lime is more soluble than limestone, several of the factors discussed in Section 2.1.3.2 are not accurate of or relevant to wet lime scrubbing. For example, reaction tank residence times are typically much shorter in lime-based systems compared to those in limestone processes. Thus lime systems have smaller hold tanks resulting in lower capital and operating costs.[70] Unlike limestone systems, which show a much higher SO_2 removal performance with simulated plug flow reactors, lime systems show little improvement with these as compared to batch reactors. The pH of the slurry at the scrubber inlet is generally around 8 to 9 for lime systems as opposed to 5-6 for limestone systems.[86] The solids from the lime based systems are not thixotropic and are much easier to dewater. Therefore, forced oxidation does little to improve the handling characteristics of the waste solids. Waste solids from lime systems are also more stable after disposing to a landfill, but still may require fixation depending on disposal site requirements.[96] The use of excess reagent is not required with lime systems because reagent utilization is typically above 95 percent.[70] Also, tests have shown that mass transfer additives such as dibasic and adipic acid, which have significantly improved the performance of limestone systems, have little if any effect on utilization or SO_2 removal for lime systems. However, magnesium oxide enhanced or Thiosorbic lime (a particularly reactive lime) has proved to be effective as will be discussed below.[96]

Thiosorbic lime - Thiosorbic lime is a unique type of lime with a high magnesium concentration (typically around 4 to 8 weight percent MgO). Currently, a mine in Maysville, Kentucky is the only natural source of Thiosorbic lime in the United States.[97,98] Dravo Lime Company owns the Maysville facility and has patents on all Thiosorbic lime systems, both natural and synthetic. Since MgO is about 600 times more soluble in water than corresponding calcium compounds, the amount of available alkalinity in the scrubbing solution is increased with its use.[99] Thus, for the same system configuration, SO_2 removal efficiency will increase (over 90% SO_2 removal has been achieved). On the other hand, use of Thiosorbic lime will reduce the required L/G ratio (and associated pumping costs) for a constant SO_2 efficiency target. In addition, reliabilities have been substantially higher due to a reduction in scaling. This is partially because MgO enhances buffering in a pH range of 5.8 - 6.5, well below the pH at which the onset of scaling occurs. Although waste disposal problems might be anticipated with a more soluble reagent, the supplier states that 45-50% solid sludges are routinely attained.[97,98]

2.1.4.3 Applicability to industrial boilers. Lime processes have found only limited application on industrial boilers and, like limestone systems, are more applicable to larger utility size boilers for the same reasons described in Section 2.1.3.3. The March 1982 Background Information Document had reported three industrial wet lime systems in operation (Table 2.1-13). However, it was found out that Carborundum Abrasives scrubs only for particulate matter and has always burned a compliance coal to meet SO_2 regulations.[100] The Armco Steel plant took its lime scrubber out of operation around 1979-1980. The boiler on which it is installed currently uses process waste gas when it is called upon to operate.[101] The system at Pfizer, which was developed by Pfizer and the National Lime Association, is still operating. It should be noted that at least part of the reason for installing a lime FGD system at Pfizer was to take advantage of the chemical properties of the scrubber blowdown. This slurry stream, which has a solids content of about 4 weight percent, is pumped to the plant's industrial wastewater pretreatment unit. There, it is used to neutralize the wastewater and precipitate metal ions generated by other processes within the plant. The resulting sludge is concentrated in a vacuum filter and hauled to a non-hazardous waste landfill.[95]

In contrast to the limited application of wet lime FGD systems in the industrial boiler sector, lime systems are the second most prevalent type of FGD system for utility boilers. As of November 1982, 35 lime systems were installed on utility boilers, representing approximately 18 percent of the total number of utility FGD systems.[84]

2.1.4.4 Development Status. The lime wet scrubbing technology is well established in the utility industry. Currently, several efforts are focused on ways to improve reliability. For example, as with utility limestone systems, lime systems are beginning to use spray towers to increase reliability while maintaining, if not improving, SO_2 removal efficiency (see Section 2.1.4.2). Of the six utility lime systems scheduled to begin operation in the 1982-1984 period, the majority will have spray towers.

TABLE 2.1-13. SUMMARY OF WET LIME FGD SYSTEMS INSTALLED ON U. S. INDUSTRIAL BOILERS AS OF OCTOBER 1983

Process	Vendor	Company/Location	Start-up Date	Number Of FGD Units	Size (acfm)	Fuel Type	Fuel Sulfur (%)	Current Status
Lime	In-house design	Pfizer, Inc. East St. Louis, IL[84]	1978	1	100,000	Coal	3.6	Operational
Lime	Koch Engineering	Armco Steel Middletown, OH[53,101]	1975	1	140,000	Coal	1.0 - 1.2	Shut down
Lime	Carborundum	Carborundum/Abrasives Buffalo, NY[53,100]	1980	1	40,000	Coal	2.2	Uses a Compliance Coal

However, unlike limestone systems, these lime systems will be using neither mass transfer additives nor forced oxidation. This is because reagent insolubility and thixotropic sludges are not as great a concern for lime systems as they are for limestone systems.[96]

There are currently 13 utility FGD systems using Thiosorbic lime, all located in the Ohio River Valley. These plants along with other pertinent information are listed in Table 2.1-14.[98] As the table shows, availability figures for these systems are about 95 percent on average. A number of studies have shown 10-15 percent lower capital investment costs and lower operating costs using Thiosorbic lime over comparable limestone scrubber systems for electric utility plants.[98]

The Pfizer plant does not currently use Thiosorbic lime. However, Thiosorbic lime is being used in the industrial fluidized bed combustion units at the Ashland Petroleum plant in Catlettsburg Kentucky.[97]

2.1.4.5 Reliability. Reliability of lime FGD systems for industrial boiler applications is difficult to assess because of little available data. The one industrial application reports an availability of 95 percent. According to the plant, the only major problem encountered with this system has been plugging of the scrubber's inlet and outlet gas ducts.[95]

Although there is a paucity of reliability information for industrial wet lime systems, a substantial data base exists for utility installations. In a study performed for the EPA using this data base, 23 lime systems were evaluated. The lime systems were reported as having an average availability of 84.1 percent and an average operability of 75.4 percent.[64] As with the limestone systems, the primary components of failure were dampers, duct systems, fans, absorber towers, and mist eliminators;[64] yet significant improvements can also be expected with improved design, operating and maintenance. Nevertheless, wet lime FGD systems are not expected to be able to compete with sodium-based FGD systems in the industrial market for the same reasons discussed in Section 2.1.3.5 for limestone systems.

TABLE 2.1-14. THIOSORBIC LIME APPLICATIONS TO UTILITY BOILER FGD SYSTEMS [98]

Plant/Location	Size (MW_e)	Startup	Coal S Content (Wt. %)	Type of Scrubber	Operating L/G (Gal/10^3 acf)	Design SO_2 Removal Efficiency (%)	Availability Index (%)
BIG RIVERS							
Green 1	242	12/79	3.75	Spray	40	90	93.0
Green 2 (at Sebree, Ky.)	242	11/80	3.75	Spray	40	90	96.3
CINCINNATI GAS & ELECTRIC							
East Bend 2 (at Rabbit Hash, Ky.)	650	3/81	3.0	Tray	33	87	90+
COLUMBUS & SOUTHERN OHIO							
Conesville 5	411	1/77	4.7	Tray	55	89.5	96.6
Conesville 5 (at Conesville, Oh.)	411	6/78	4.7	Tray	55	89.6	89.9
MONONGAHELA POWER							
Pleasants 1	618	3/79	3.0	Tray	45	90	90+
Pleasants 2 (at Willow Island, W. Va.)	618	10/80	3.0	Tray	45	90	90+
PENN POWER							
Bruce Mansfield 1	917	12/75	3.0	2-Stage Venturi	70	92	98.5
Bruce Mansfield 2	917	7/77	3.0	2-Stage Venturi	70	92	97.9
Bruce Mansfield 3 (at Shippingport, Pa.)	917	6/80	3.0	Horizontal Spray	75	92	97.2
DUQUESNE LIGHT							
*Phillips (at South Heights, Pa.)	408	3/78	2.2	Venturi	35	83	98.0
*Elrama (at W. Elizabeth, Pa.)	510	4/78	2.2	Venturi	35	83	94.4
WEST PENN POWER							
Mitchell (at Courtney, Pa.)	300	8/82	2.8	Spray	-	95+	-

*Currently achieving less than 0.6 lb/MMBTU on a continuous monitor.

2.1.4.6. Emissions data. Industrial lime systems have achieved over 90 percent SO_2 removal efficiency. In a 30-day test at the RANGB FGD system using lime as a reagent and operating on a 3.5 percent sulfur coal, the SO_2 removal efficiency was 91.5 percent. The actual emissions were 0.4 lb $SO_2/10^6$.[66] Pfizer has reported an SO_2 removal efficiency for its system to be above 90 percent for 3.5 percent sulfur coal; however, the actual SO_2 removal efficiency was not given, nor was the method used for determining it.

2.2 DRY PROCESSES

Dry processes that have potential applicability to industrial boilers include spray drying of a lime or sodium reagent, dry injection of a sodium reagent, electron-beam irradiation of flue gas containing ammonia or lime and combustion of a pelletized or pulverized coal and limestone mixture. Each of these processes results in a dry product for waste disposal. The use of the coal/limestone fuel mixture is discussed in Section 4.2.

2.2.1 Spray Drying

Spray drying FGD technology has developed rapidly over the past several years and is an applicable SO_2 control method for all industrial boilers. The technology is offered by more than 10 system vendors and 21 industrial spray drying units have been sold. Seven of these units are currently operational.

Spray drying involves contacting the flue gas with an atomized lime slurry or a solution of sodium carbonate. The hot flue gas dries the droplets to form a dry waste product while the absorbent reacts with SO_2 in the flue gas. The dry waste solids, consisting of sulfite and sulfate salts, unreacted absorbent and fly ash, are collected in a baghouse or ESP for disposal.

2.2.1.1 Process description. A schematic diagram of the spray drying FGD process is shown in Figure 2.2-1. Flue gas containing fly ash and SO_2 enters the spray dryer and is contacted with a finely atomized alkaline solution or slurry. During the approximately 10-second residence time in the dryer, the flue gas is adiabatically humidified as the water in the slurry or solution is evaporated. Simultaneously, flue gas SO_2 reacts with the alkaline species to form solid sulfite and sulfate salts. The solids formed are dried to generally less than 1 percent free moisture. The flue gas, which has been humidified to within 11 to 28°C (20 to 50°F) of its

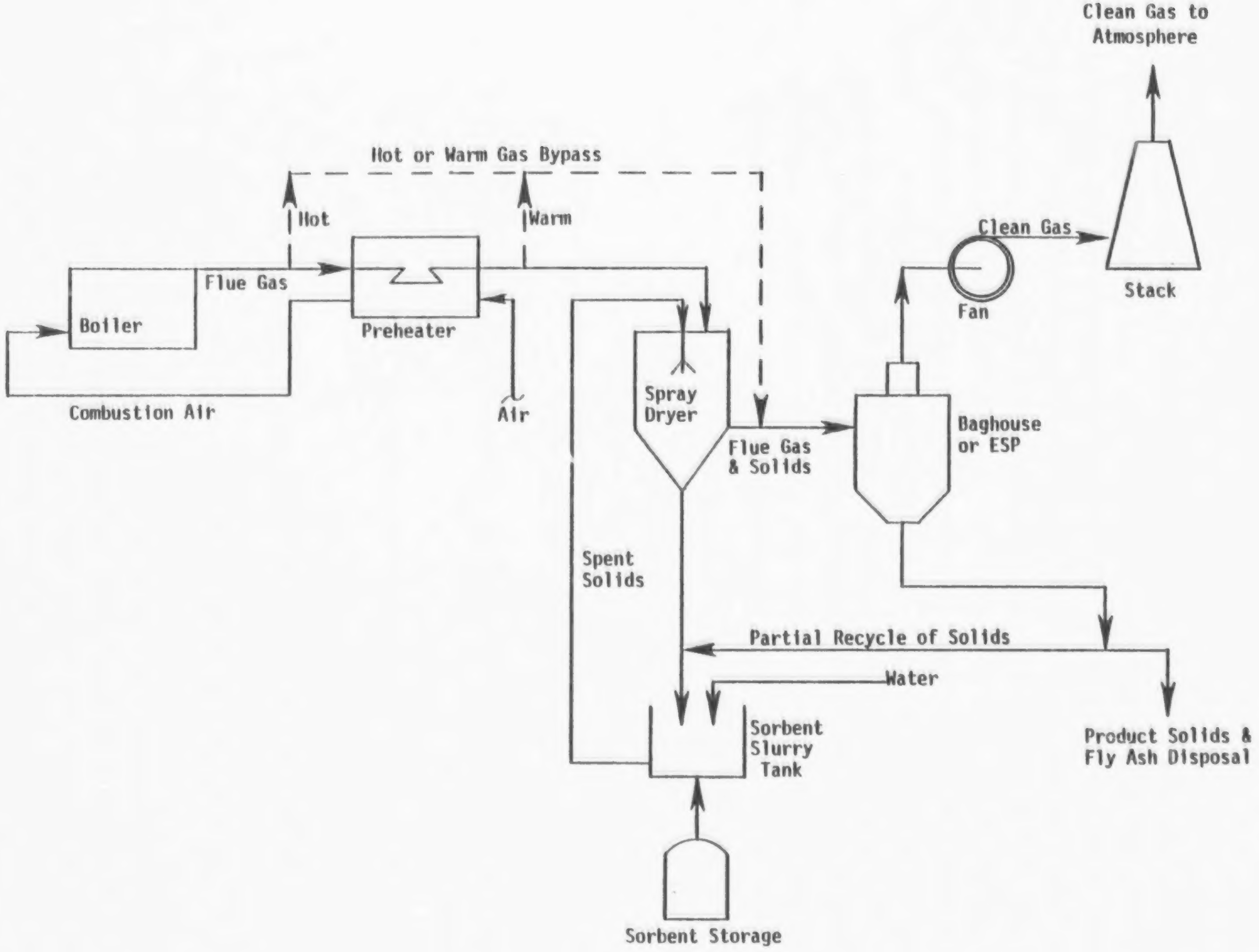


Figure 2.2-1. Typical Spray Dryer/Particulate Collection Flow Diagram

adiabatic saturation temperature, passes through the dryer and into a high efficiency particulate matter control device. In some system designs a portion of the solids drops out of the dryer, but the bulk of the desulfurization products are collected with fly ash in a baghouse or an ESP. The most common reagent is lime, although sodium-based reagents are also used. Atomization designs vary with regard to the use of rotary disk or two-fluid nozzle atomizers, wheel speed in rotary atomizers, external or internal mixing in nozzle atomizers and the number of atomizers per dryer.

The reaction between the alkaline material and flue gas SO_2 continues as the gas passes through the ductwork and the baghouse or ESP. Reaction mechanisms and mathematical models have been postulated for the lime spray dryer process.[102,103] The overall chemical reactions for lime and sodium carbonate are shown below.

$$SO_2 + CaO + 1/2\ H_2O \longrightarrow CaSO_3\ \ 1/2\ H_2O \qquad (2.2\text{-}1)$$

or

$$SO_2 + Na_2CO_3 \longrightarrow Na_2SO_3 + CO_2 \qquad (2.2\text{-}2)$$

In addition to these primary reactions, sulfate salts are produced by the following reactions:

$$SO_2 + CaO + 1/2\ O_2 + 2H_2O \longrightarrow CaSO_4\ \ 2H_2O \qquad (2.2\text{-}3)$$

or

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4 \qquad (2.2\text{-}4)$$

$$SO_3 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 \qquad (2.2\text{-}5)$$

Auxiliary equipment associated with the spray drying process includes a reagent preparation system. Sodium carbonate reagent is prepared as a concentrated solution in a stirred tank. In lime systems, pebble lime is generally slaked in ball mill, paste or detention slakers, although ball mill and paste slakers are more common.

Reagent utilization can often be improved by recycle of the waste solids, particularly in lime systems, where the unreacted reagent in the waste solids can be reused. The recycle solids are either slurried separately and added to the reagent feed just upstream of the spray dryer or they are added directly to the fresh reagent holding tank.[103,104] Additional advantages to the use of solids recycle include (1) a more easily dried atomizer slurry because of a higher initial weight percent solids and (2) reduced scaling potential compared to once-through lime systems with feed slurries containing less than 10 percent solids.[105,106] Disadvantages to solids recycle include the added capital costs and operating complexity associated with the solids recycle equipment. Solids recycle may not be used on some systems, depending on the amount of unreacted reagent in the waste solids and vendor or operator preference.

2.2.1.2 Factors affecting performance. The performance of a spray dryer FGD system depends on several factors, the two most important being the flue gas approach to saturation temperature at the dryer outlet and the amount of reagent added per unit of inlet SO_2 (reagent ratio). Unlike wet scrubbing systems, the amount of water that can be added to the flue gas (the L/G ratio) is set by heat balance considerations for a given inlet flue gas temperature and approach to saturation. Typical L/G ratios range from 0.03 to 0.04 ℓ/m^3 (0.2 to 0.3 $gal/1000\ ft^3$). The amount of reagent added (reagent ratio) is varied by raising or lowering the concentration of a solution (sodium system) or weight percent solids of a slurry (lime system) containing this set amount of water. While holding other parameters such as temperature constant, SO_2 removal increases with increasing reagent ratio. However, as the reagent ratio is increased to raise the level of SO_2 removal, two limiting factors are approached:

- Reagent utilization decreases, raising reagent and disposal costs.
- An upper limit is reached for the solubility of the reagent in the solution, or for the weight percent of solids in the slurry (due to pumpability considerations).

There are at least two methods of circumventing these limitations. One method is to utilize solids recycle, using the solids that have dropped out in the spray dryer or collected in the particulate emission control device. Recycle has the advantage of increasing reagent utilization, and it can also increase the opportunity for utilization of any alkalinity in the fly ash.[104]

The second method of avoiding the above limitations on SO_2 removal is to operate the spray dryer at a lower outlet temperature; that is, a closer approach to saturation. Operating the spray dryer at a closer approach to saturation has the effect of increasing both the residence time of the liquid droplets and the residual moisture level in the dried solids. As the approach to saturation is narrowed, SO_2 removal and reagent utilization increase dramatically.[104]

The approach to saturation at the spray dryer outlet is set by either the requirement for a margin of safety to avoid condensation in downstream equipment or restrictions on stack temperature. The design approach to saturation for spray drying systems generally ranges from 10 to 28°C (18 to 50°F). Operation at a relatively close approach to saturation, 10 to 14°C (18 to 25°F), is common for applications where SO_2 removal requirements approach 85 to 90 percent. However, operation at a close approach to saturation may also be used to decrease reagent use in lower efficiency applications.

Some spray dryer system designs, particularly on large utility boilers, allow for warm or hot gas bypass around the spray dryer to reheat the dryer outlet gas (see Figure 2.2-1). Warm gas (from downstream of the boiler air heater) can be used at no energy penalty, while the use of hot gas (upstream of the air heater) has an energy penalty associated with the decrease in energy available for air preheat.

Another factor that may affect the performance of spray drying systems is the inlet flue gas temperature. For inlet flue gas temperatures significantly below approximately 121°C (250°F), SO_2 removal may be limited by the amount of water and reagent that can be added to the flue gas. The limiting inlet temperature for a particular system depends on the fuel sulfur content, desired SO_2 removal and reagent quality.

Spray dryer system performance can also be affected by the choice of the particulate collection device. Baghouses have been chosen over ESP's in most commercial spray drying applications. Baghouses have an advantage over ESP's in that unreacted alkalinity in the solids and fly ash collected on the filter bag surface can react with the remaining SO_2 in the flue gas as the gas passes through the baghouse. Pilot studies have shown that SO_2 removal across the baghouse may account for 15 to 20 percent of the overall SO_2 removal, depending on reagent ratio, approach temperature and baghouse pressure drop.[107] Data from recent tests on a full-scale (110 MWe) utility system show baghouse SO_2 removals ranging from 9 to 10 percent of overall removal during low sulfur (1.2 percent) coal testing and 13 to 15 percent during high sulfur (3.5 percent) tests. Overall SO_2 removal during these tests was 90 percent and the system operated at a 10°C (18°F) approach to saturation.[108]

The factors that are important in making the choice between ESP's and fabric filters include:

- Use of solids recycle (increased dust loading increases the size and cost of an ESP).
- Fly ash resistivity (high ash resistivity often requires larger, more expensive ESP's).
- Pressure drop considerations (an ESP will result in lower pressure drop costs than a fabric filter).

Baghouse designs for spray dryer applications vary primarily with regard to bag fabric, cleaning frequency and cleaning mode. Thirteen of the 21 industrial spray drying units sold will use pulse-jet baghouses; the others will use reverse-air baghouses.

2.2.1.3 Applicability to industrial boilers. Spray drying FGD is an applicable SO_2 control method for all industrial boilers. Early development work on spray drying systems demonstrated applicability to boilers firing low to medium sulfur fuels (less than 3 percent sulfur).[109] Recent test results reported for two industrial spray drying systems and a small utility system (100 MWe) show that the SO_2 control method is applicable to high sulfur (3 to 4 percent sulfur) fuels as well.

For spray drying systems using sodium carbonate as the reagent, disposal of the waste product may entail additional requirements. The waste consists of highly soluble sodium salts, such as Na_2SO_3 and Na_2SO_4. Land disposal of the waste solids may require clay- and/or plastic-lined landfills in areas where the potential exists for groundwater contamination. All industrial boiler spray drying systems sold so far will be or are currently using lime as the reagent.

2.2.1.4 Development status. Spray drying technology for removing SO_2 from boiler flue gas has developed rapidly over the past several years. The technology is commercially offered by more than 10 system vendors and 21 spray drying FGD units have been sold for industrial boiler applications. Seven of these units are currently operational and four other units are expected to be in start-up by the end of 1983.

The commercial systems sold for industrial boiler applications are summarized in Table 2.2-1. These systems are being applied to boilers burning coals with a fairly wide range of sulfur contents (0.6 to 3.5 percent sulfur). The systems have SO_2 removal guarantees ranging from 70 to 90 percent and at least five of the systems have outlet SO_2 emission guarantees for a maximum of 520 ng/J (1.2 lb/10^6 Btu) or lower.[3]

In addition to the systems for industrial boilers, 17 utility spray drying systems have been sold. The applications range in size from 44 to 860 MWe and total about 6,800 MWe in FGD system capacity. The utility systems are being applied to low sulfur (less than 2 percent) coal-fired units and SO_2 removal guarantees from the vendors are as high as 90 percent. Six of the utility systems are operational and one system is in the initial startup stages.[110-113]

TABLE 2.2-1. SUMMARY OF INDUSTRIAL BOILER SPRAY DRYING SYSTEMS[113]

System Purchaser/Location	Vendor[a]	Size, Mg/hr (lb/hr) Steam	Coal Data		SO_2 Removal Guarantee[c]		Startup Date/Status[d]
			Type	Sulfur	Removal	Outlet (lb/10^6 Btu)	
Argonne National Laboratory Argonne, IL	Niro/Joy	77 (170,000)	Illinois bituminous	3.5%	78.7%	1.2	Operational. Turned over to purchaser.
Strathmore Paper Company Woronoco, MA	Mikropul/Koch Engineering	39 (85,000)	Eastern bituminous	2.3 to 3%	75%	1.2	Operational. Turned over to purchaser.
Celanese Fiber Company Cumberland, MD	Rockwell Int./ Wheelabrator-Frye	50 (110,000)	Eastern subbituminous	2% maximum	70% for 1% S coal; 86% for 2% S coal	70 lb/hr SO_2 outlet	Operational. Turned over to purchaser.
Container Corporation Philadelphia, PA	Ecolaire, Inc.	77 (170,000)	Eastern subbituminous	1%	Design removal of 90%	NA[e]	Operational. Turned over to purchaser.
University of Minnesota: Units 1 & 2 Minneapolis, MN	Flakt, Inc.	40 MWe[b]	Subbituminous each	0.6 to 0.7%	70%[f]	NA	One unit operational; second startup in September 1983.
Austell Box Board Co. Austell, Georgia	Wheelabrator-Frye	114 (250,000)	Bituminous	1.0 to 2.5%	Varies with sulfur content	1.2	Operational. Not turned over to purchaser.
General Motors Buick Division Flint, MI	Niro/Joy	204 (450,000)	Indiana bituminous	1 to 3%	70 to 90%	1.2	Operational. Not turned over to purchaser.
Fairchild Air Force Base: Units 1, 2, & 3 Spokane, WA	Niro/Joy	50 (110,000)	Western subbituminous	1%	85%	NA	Initial startup stages.
Puget Sound Naval Shipyard: Units 1, 2, & 3 Bremerton, WA	G. E. Environmental Services	64 (140,000) each	NA	1.6% maximum	84%	NA	Late 1987.
Maelstrom AFB: Units 1, 2 & 3 Grent Falls, MT	Niro/Joy	41 (90,000) hot water each	Western subbituminous	1.0%	85%	NA	Spring 1985.
Griffis AFB Units 1,2,3 & 4 Rome, NY	Ecolaire, Inc.	41 (90,000) each	Eastern bituminous	3.0%	85%	0.71	Late 1984

[a] Niro/Joy = Niro Atomizer Inc./Joy Western Precipitation Division.

[b] Electrical output, part of cogeneration system.

[c] Where guarantee information not available, design values are reported.

[d] As of October 1983.

[e] NA = not available.

[f] At reagent ratio of 1.0.

2.2.1.5 Reliability. Reliability of industrial spray drying systems is difficult to assess because only four systems have been operational for a long period of time. These are operated by Strathmore Paper, Celanese Fibers, Argonne National Lab and Container Corporation. The data available indicate that lime spray drying FGD systems applied to industrial units are reliable when operating at SO_2 removal efficiencies in the 60 to 75 percent range on both bituminous and subbituminous coals of 3 weight percent sulfur or less.

Availability of the spray dryer system at the Strathmore Paper Company has been quite high except during the early stages of operation. Availability is defined as the percentage of hours that the FGD system is available for operation (whether used or not) divided by the hours in the period. Initial startup problems in late 1979 resulted in significant amounts of downtime. These problems were a result of poor initial spray dryer design combined with an actual gas flow that was 25 to 35 percent higher than the design flow. However, following system design modifications in March 1980, the system operated for nearly 1.5 years with approximately 80 percent overall system availability while achieving 70 percent SO_2 removal on a bituminous coal of 3.0 weight percent sulfur. Strathmore subsequently switched to a low sulfur coal, 1 percent, and lowered the SO_2 removal to 60 percent. The system has operated in this mode for 1.5 years and experienced 94 percent availability during this period.[114] The system normally operates 24 hours per day throughout the year. Sudden and wide variations in boiler load are common at the plant because of changes in process steam demand. These load changes are reported to have little effect on the spray drying system and downstream baghouse.[115]

The spray dryer system at the Celanese Fibers Company also showed relatively low availability (65 percent) during the early stages of operation. Initial operating problems were related to variable coal quality, slurry feed pump wear, ineffective grit removal and atomizer slurry maldistribution. Solution of these problems required minor modifications in system design and operation.[116] Following these modifications, system availability averaged between 90 and 95 percent for the period from October

1980 to mid-1982.[113,116] During this period the FGD system averaged 70 percent SO_2 removal on a subbituminous coal with an average 1.0 weight percent sulfur content. Solids recycle was not employed at this site but a fabric filter was used for particulate matter control.

Startup of the Argonne National Laboratory system began in November 1981 and the system was fully operational in February 1982. Problems encountered during the startup involved auxiliary equipment such as slurry pumps, agitators and blowers.[117] During the past year, the system has operated with approximately 80 to 85 percent availability, while achieving about 80 percent SO_2 removal on a 3.5 weight percent sulfur coal, excluding two major down periods. If these two major down periods are included the availability drops to 56 percent. The first down period resulted from delamination of 40 percent of the filter bags after nine months of operation. These felted fiberglass bags were replaced with woven fiberglass bags. The other major down period was also the result of a baghouse failure. This facility is the only one of the four to operate with solids recycle.

The spray drying system at Container Corporation of America has operated for 2.5 years achieving 75 percent SO_2 removal with 0.6 percent sulfur coal. The availability has steadily increased since start-up and the overall availability during this period has been 80 percent. The primary operating problem has involved failure of the atomizer. The plant keeps a spare atomizer on site and can change atomizers very quickly thereby minimizing downtime.[114]

2.2.1.6 Emission Data. Recently available emissions test data for four industrial spray drying systems are shown in Table 2.2-2. As shown in Table 2.2-2, outlet SO_2 emission rates of less than 366 ng/J (0.85 lb/10^6 Btu) were achieved with all four systems. Results of short-term tests show SO_2 removal efficiencies above 90 percent were achieved at locations A, B, and D for coals ranging from 0.6 percent to 3.8 percent sulfur. No long-term continuous monitoring data for these systems are currently available. Comparison of the data presented for locations A and B shows a

TABLE 2.2-2. SUMMARY OF EMISSION DATA FOR FOUR INDUSTRIAL LIME SPRAY DRYING FGD SYSTEMS

		EPA Method 6 Test Results								
Location	No. of Runs	Inlet SO_2 (ng/J)[a] Average	Outlet SO_2 (ng/J)[a] Range	Outlet SO_2 (ng/J)[a] Average	% SO_2 Removal Average	Boiler Load	Reagent Ratio[b]	Coal Sulfur Content	Approach Temperature °C (°F)	Solids Recycle Rate (kg Solids/ kg Lime Feed)
A	3	2,877	NA[c]	585	79.7	35%	0.8	3.0%	13 (23)	2:1
A	3	2,550	NA	258	89.9	70%	1.5	3.0%	13 (23)	2:1
A	3	2,630	NA	116	95.6	82%	2.0	3.0%	13 (23)	2:1
B	6	2,316	NA	176	92.4	75%	1.9	3.8%[d]	14 (25)	None
C	6	1,430[e]	323 - 452	366	74[f]	100%	NA	1.5 - 2.5%	19 (35)	None
D	3	516[e]	12.5 - 17.2	14.3	97.2[f]	NA	NA	0.6%	NA	None

[a] Divide by 430 to convert to lb/10^6 Btu.

[b] Moles of calcium per mole of inlet SO_2.

[c] NA = not available.

[d] Coal/oil mixture with 94.2% coal heat input.

[e] Estimated from coal properties.

[f] Estimated from coal properties and measured outlet emission rate.

considerably lower reagent requirement to achieve 90 percent SO_2 removal on the system with solids recycle. This is expected since the use of solids recycle improves reagent utilization.

2.2.2 Dry Alkali Injection

In the dry injection process, a dry alkaline material is injected into the flue gas just ahead of a particulate control device. The alkaline material reacts with the SO_2 in the flue gas and the solids and fly ash are collected for disposal.

Dry injection technology has been developed through pilot and laboratory scale studies but is not yet commercially applied to industrial boilers. Application of the technology is planned, however, for a 500 MWe utility boiler.

2.2.2.1 Process description. A generalized flow diagram of the dry alkali injection process is shown in Figure 2.2-2. Dry injection schemes generally involve pnuematic injection of a dry, powdery sodium-based reagent into the flue gas with subsequent particulate collection in a baghouse. The point of alkali injection has been varied from the boiler furnace all the way to the inlet of the baghouse. Although other alkaline reagents, such as lime, limestone and magnesium dioxide, have been tested, only certain sodium compounds have shown the capability for high SO_2 removal from the flue gas.[3] Both baghouse and ESP collection devices have been tested with dry injection processes. However, the effect of the reaction between unspent reagent on the filter bag surface and SO_2 remaining in the flue gas seems overwhelmingly to favor the bag collector.

Nahcolite and trona ores, which contain naturally occurring sodium compounds appear to be the most promising reagents for dry injection in terms of reactivity and cost.[119,120] Nahcolite, which contains 70 to 90 percent sodium bicarbonate ($NaHCO_3$) has been shown to be more reactive with SO_2 in flue gas than trona ore (Na_2CO_3 $NaHCO_3$ $2H_2O$).[121,122]

The principle reaction product from nahcolite and trona injection is sodium sulfate (Na_2SO_4), according to the following overall reactions:[123,124]

$$2NaHCO_3 + SO_2 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 + 2CO_2 + H_2O \qquad (2.2.3)$$

$$2(Na_2CO_3 \;\; NaHCO_3 \;\; 2H_2O) + 3SO_2 + 3/2\ O_2 \longrightarrow 3Na_2SO_4 + 4CO_2 + 5H_2O \qquad (2.2.4)$$

Prior to reaction with SO_2, it appears that both nahcolite and trona must undergo a decomposition step as shown below.[125]

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad (2.2.5)$$

$$2(Na_2CO_3 \;\; NaHCO_3 \;\; 2H_2O) \longrightarrow 3Na_2CO_3 + CO_2 + 5H_2O \qquad (2.2.6)$$

The decomposition reaction increases the porosity and reactive surface area of the reagent particles. The SO_2 reaction proceeds as follows:

$$Na_2CO_3 + SO_2 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 + CO_2 \qquad (2.2.7)$$

2.2.2.2 Factors Affecting Performance. In addition to reagent type, major factors affecting SO_2 removal by dry injection include the amount of reagent added (stoichiometric ratio), the temperature at the point of injection and the size of the reagent particles.[126]

As expected, the removal of SO_2 by dry injection increases with increasing "normalized stoichiometric ratio" (equivalent moles of Na_2O per mole of inlet SO_2) because additional reagent is available to react with the SO_2. However, higher stoichiometric ratios also result in lower reagent utilization.[126]

Nahcolite and trona undergo a decomposition prior to reaction with SO_2; the temperature at the point of reagent injection affects the rate of this decomposition. In general, injection at higher temperature increases the

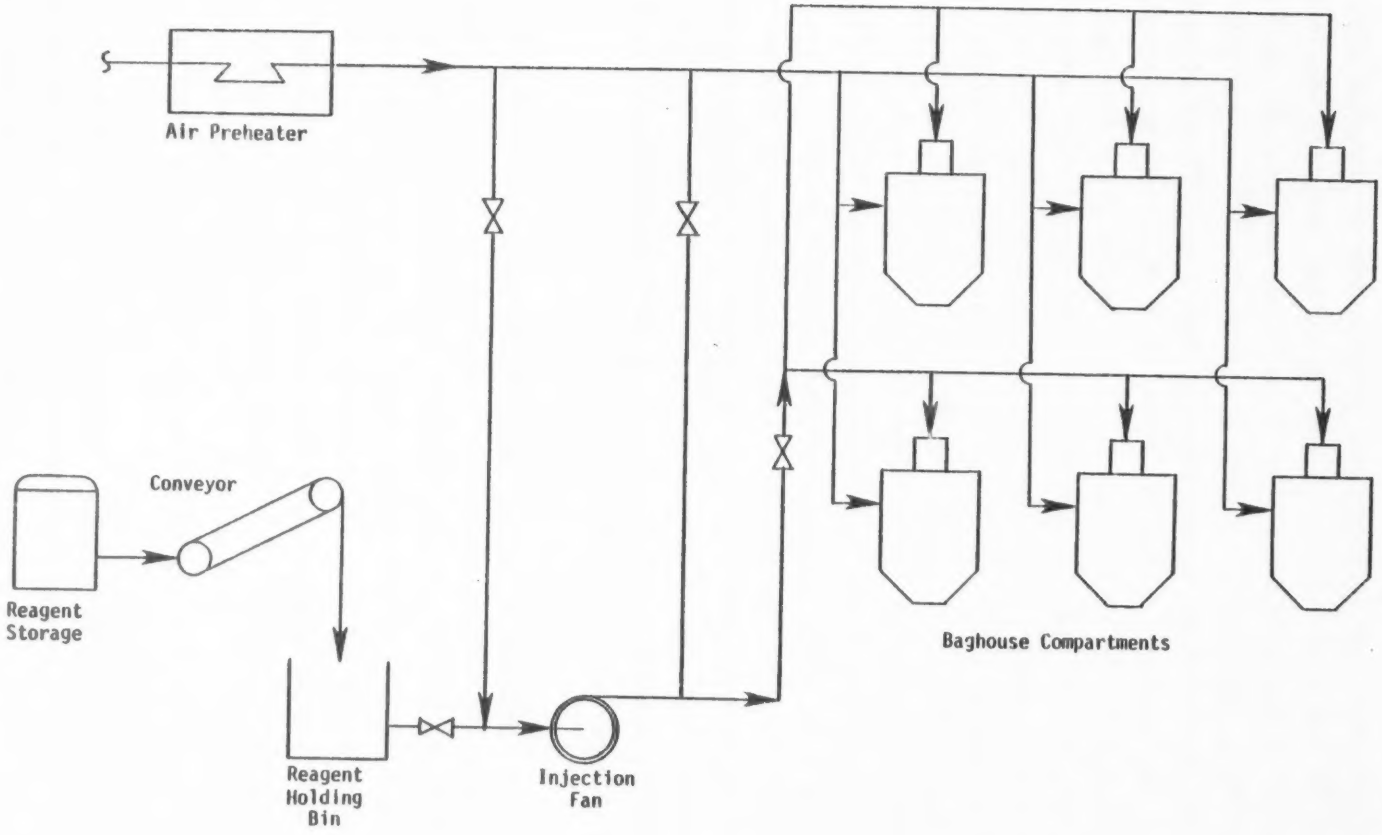


Figure 2.2-2. Dry Alkali Injection Flow Diagram

decomposition rate and increases the initial rate of reaction with SO_2.[127,128] The evolution of H_2O and CO_2 during decomposition increases the pore volume of the particles, creating more surface area for chemical reaction and a lower resistance for SO_2 diffusion.[128] As the reaction of SO_2 and Na_2CO_3 proceeds, it appears that the pores begin to plug; the reaction then becomes limited by diffusion of SO_2 into the particle.[129]

Injection of the reagent at too low a temperature will reduce the initial rate of SO_2 reaction and may limit the overall SO_2 removal achievable with the dry injection system. For nahcolite, it appears that SO_2 removal may drop off dramatically below an injection temperature of approximately 135°C (275°F).[125] The minimum injection temperature for trona is currently unknown but is estimated to be below 93°C (200°F).[21] Injection of sodium compounds at too high a temperature (about 343°C, 650°F) reduces their reactivity due to particle sintering.[126]

Another factor affecting SO_2 removal and reagent utilization in dry injection systems is particle size. In general, pilot and laboratory scale studies have shown that higher SO_2 removals are obtained with smaller particles. The majority of these studies were conducted with particles ranging in size from 30 to 200 microns.[128]

2.2.2.3 Applicability to industrial boilers. Dry alkali injection is an applicable SO_2 control method for industrial boilers firing fuels with low to moderate sulfur contents (up to 2 percent sulfur). The applicability of dry injection to boilers firing higher sulfur fuels is difficult to assess because limited data are currently available.

As with sodium-based spray drying systems, the high solubility and leaching potential of the sodium waste solids may require special disposal handling techniques. Land disposal of the solids in clay- and/or plastic-lined landfills may be called for in areas with potential for groundwater contamination.

2.2.2.4 Development Status. Dry alkali injection technology has not yet been commercially applied to either industrial or utility boilers. However, the first planned commercial application of trona injection has been announced for a 500 MWe utility installation scheduled for startup in 1990.[130] Numerous pilot and laboratory scale studies have been conducted on the technology.[124] Demonstration scale tests were recently executed on a small utility boiler (22 MWe) firing a low-sulfur western coal (0.44 percent sulfur).[122,127] Four to eight hour tests on this system showed that SO_2 removals of 70 and 90 percent can be achieved with nahcolite at stoichiometric ratios of approximately 0.8 and 1.1 respectively. For trona ore, this same system showed SO_2 removals of 70 and 90 percent at stoichiometric ratios of 1.3 and 2.4 respectively. During the testing, the normal baghouse inlet temperature ranged from 143 to 149°C (290 to 300°F).[122,127]

The application of trona dry injection had been previously constrained by questions regarding SO_2 removal limitations and cost. However, the recent demonstration-scale studies have shown that SO_2 removal efficiencies of 70 to 80 percent can be achieved with trona on low sulfur coals at reasonable stoichiometric ratios. Trona ore is currently mined in large quantities for conversion to sodium carbonate.

The application of nahcolite dry injection has been constrained by uncertainties regarding reagent cost and availability. Nahcolite is currently not mined in the United States, but at least one firm has announced intentions to develop a nahcolite mining operation[131] and several other companies are investigating the possibility of supplying nahcolite through solution mining techniques.[125,132] However, a market commitment for a minimum of 909,000 Mg/yr (1,000,000 ton/yr) of nahcolite may be necessary to off-set the large capital investment associated with opening a commercial mine.[133,134] This production level corresponds to the nahcolite demand of 5000 MWe of utility generating capacity burning 1 percent sulfur coal with 70 percent SO_2 removal.[128]

2.2.2.5 Reliability. Since dry alkali injection has not yet been commercially applied, no data are available on the reliability or operability of these systems. However, due to their inherent mechanical and chemical simplicity, dry injection systems are expected to be at least as reliable and operable as wet scrubbing systems and spray drying systems.

2.2.3 Electron-beam Irradiation

Electron-beam (E-beam) irradiation processes are still in the very early stages of development. These processes involve the irradiation of flue gas containing a reactant, such as ammonia or lime. The process removes both SO_2 and NO_x from the flue gas and produces a dry waste product that must be subsequently removed in a particulate collector.

2.2.3.1 Process description. A schematic diagram of the E-beam/ammonia process is shown in Figure 2.2-3. In this process, incoming flue gas is cooled and humidified in a water quench tower, resulting in a gas moisture content of about 10 percent. Ammonia is injected into the cooled gas and the gas is passed through an E-beam reactor. In the reactor, oxygen and water are ionized to form the radicals [HO], [O] and [HO_2] by the application of electrons at a dose of 1 to 3 Mrads (1 Mrad is equivalent to 10 joules/g of flue gas). These radicals react with SO_2 and NO_x to form sulfuric acid (H_2SO_4) and nitric acid (HNO_3). The acids are neutralized by ammonia and water in the flue gas to form solid ammonium sulfate ($(NH_4)_2SO_4$) and ammonium sulfate nitrate ($(NH_4)_2SO_4$ 2 NH_4NO_3). The reaction time for formation of the sulfate and nitrate salts is less than one second. Product solids are collected in a hopper below the E-beam reactor or in a downstream particulate collector.

In another version of the E-beam process, the water quench tower is replaced with a lime-based spray dryer (see Section 2.2.1). Reactions in the E-beam reactor occur in the same manner as above except that the products formed are calcium salts ($CaSO_4$, $Ca(NO_3)_2$ and $CaSO_3$) instead of ammonium salts.[135]

Factors impacting SO_2 and NO_x removal by electron-beam irradiation include gas moisture content, gas temperature, oxygen content, reagent ratio and electron dosage. In addition, efficient penetration of the gas stream by the beam requires a unique discharge pattern and other special design considerations.[131]

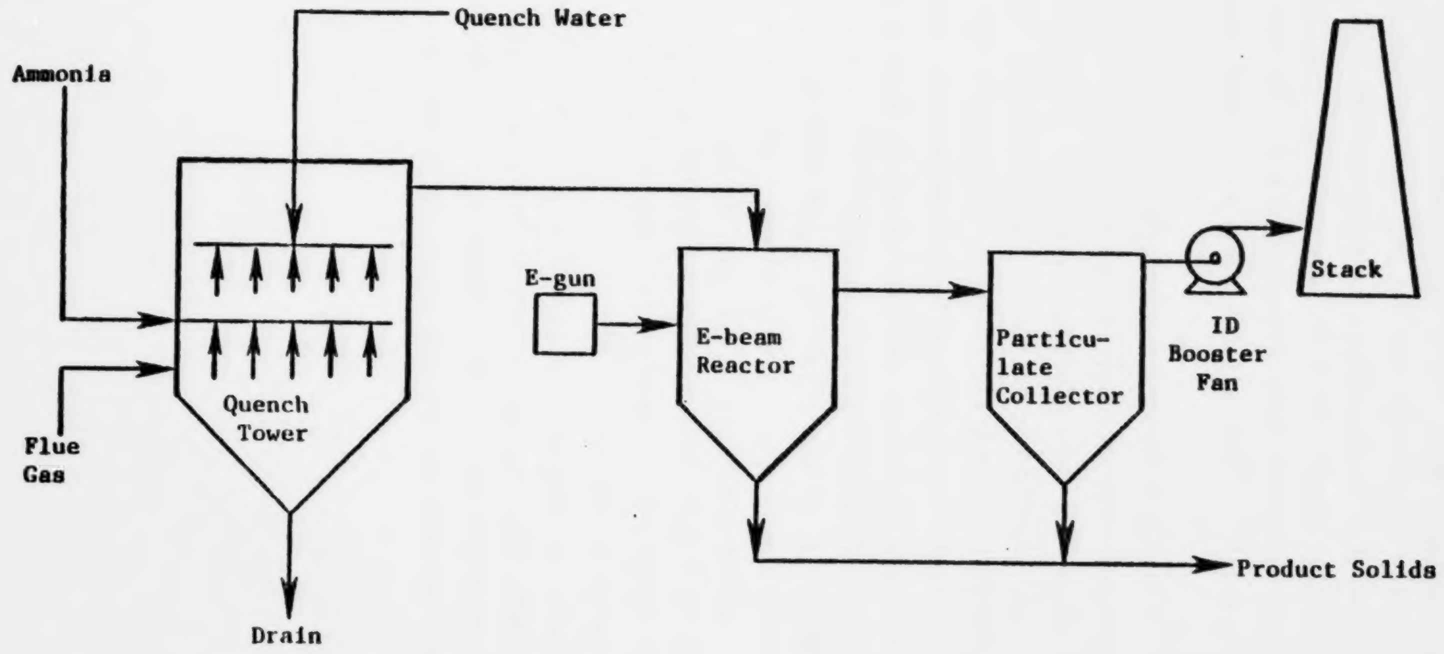


Figure 2.2-3. E-beam/ammonia process flow diagram.

2.2.3.2 Status of Development. The electron-beam process is in an early developmental state. The process has not yet been applied to a real coal-fired flue gas. However, pilot studies on both the lime and ammonia based E-beam process configurations are currently underway. The DOE has signed cost sharing agreements with both Research-Cottrell and the joint venture EBARA/Avco-Everett.[136] These pilot systems will treat flue gas from coal-fired boilers.

Research-Cottrell will evaluate the E-beam/lime slurry process with a 10,000-acfm pilot plant currently being installed at TVA.[137] NO_x and SO_2 removal optimization tests will be conducted at electron irradiation rates between 0.5 and 1.5 Mrad. During the scheduled 2-year program, Research-Cottrell will also conduct nitrate fixation tests and electron-gun cost reduction studies.[138] Research-Cottrell performed bench-scale studies on the E-beam process under DOE Funding in 1979 and recently developed a mathematical model for the E-beam/lime slurry process.[139]

EBARA/Avco-Everett will conduct 10,000 to 20,000 acfm pilot studies on the E-beam/ammonia injection process. A host site for this study is still being negotiated.[36] Current plans are to conduct the testing on flue gas from a high-sulfur eastern coal. Following optimization and reliability testing, EBARA and Avco plan to investigate the potential use of waste products from the process as fertilizer.[138]

The EBARA Manufacturing Company in conjunction with Japan Atomic Energy Research Institute (JAERI) has operated a 1000 Nm^3/hr pilot plant treating flue gas from an oil-fired boiler. In 1976, EBARA tested a 3000 Nm^3/hr pilot plant on the off-gas from an iron ore sintering furnace at Nippon Steel.[140]

2.3 REFERENCES

1. Struthers - Anderson Pollution Control Systems. Points to Consider in Evaluation of SO_2 Emission Control Systems for Steam Generators in the Oil Fields. Atlanta, Ga. November 1980. pp. 4-5, 7, 12-13, 14-15.

2. Durkin, T. H., Southern Indiana Gas and Electric Company, et al. Operating Experience with a Concentrated Alkali Process. (Presented at the American Power Conference, 1980).

3. Memo from Berry, R. S., Radian Corporation, to Charlie Sedman and list of Addresses. November 11, 1983. Notes from September 8 meeting with Jack Brady of Andersen 2000 and from subsequent phone conversations with him.

4. Memo from Shareef, G. S., and Berry, R. S., Radian Corporation, to the Industrial Boiler SO_2 Docket. December 30, 1983. Development of Material Balance for the Sodium Scrubbing FGD Algorithm.

5. Memo from Berry, R. S., and Maddox, J. A., to the Industrial Boiler SO_2 Docket. February 15, 1984. Sodium Scrubber Data Sample and Analysis.

6. Oestreich, D. K. Equilibrium Partial Pressure of Sulfur Dioxide in Alkaline Scrubbing Processes. (Prepared for the U.S. Environmental Protection Agency, Office of Research and Development.) Washington, DC. Publication No. EPA600/2-76-279. October 1976. p. 13.

7. Technical Note from Berry, R. S., Radian Corporation, to the Industrial Boiler SO_2 Docket. May 31, 1984. SO_2 Re-emissions from the Sodium Scrubbing Wastewater Stream in Aerobic Environments. Chapter 3.

8. Technical Note from Berry, R. S., Radian Corporation, to the Industrial Boiler SO_2 Docket. January 25, 1984. Update of the Sodium Scrubber Wastewater Issue. p. 6.

9. Brady, J. D., Andersen 2000. Particulate and SO_2 Removal with Wet Scrubbers. Chemical Engineering Progress. pp. 73-77. June 1982.

10. Letter from Mayrsohn, H., Kern County Air Pollution Control District, to Berry, R. S., Radian Corporation. August 9, 1983. Sodium Scrubber Source Data.

11. Reference 1, p. 7.

12. Reference 1, pp. 4-5.

13. Reference 1, pp. 12-13.

14. Letter from Clum, D. N., Heater Technology, to Berry R. S., Radian Corporation. August 5, 1983. Heater Technology Response to Radian's Letter.

15. Cornell, C. G., and Dahlstrom, D. A., Environtech. Sulfur Dioxide Removal in a Double Alkali Plant. Chemical Engineering Progress. pp. 47-53. December 1973.

16. Brady, J. D., Struthers - Andersen Pollution Control Systems Emission Control for Oil-Fired Steam Generators. Atlanta, GA. November 14, 1979. pp. 19, 30.

17. Memo from Berry, R. S., Radian Corporation, to Meeting Attendees and Durkee, K. R., EPA. July 1, 1983. Revised notes from June 7, 1983 FMC meeting on the Dual Alkali Technology.

18. Letter from Seipp, D. D., FMC-Wyoming, to Berry, R. S., Radian Corporation. August 11, 1983. Response to sodium scrubbing letter.

19. Letter from Cameron, H., General Motors, to Berry, R. S., Radian Corporation. October 20, 1983. Response to sodium scrubbing letter.

20. Letter from Brady, J. D., Andersen 2000, to Berry, R. S., Radian Corporation. July 28, 1983. Response to sodium scrubbing letter.

21. Letter from Anderson, D. F., Grace Petroleum to Berry, R. S., Radian Corporation. October 10, 1983. Response to sodium scrubbing letter.

22. Letter from Souza, M., Bradford Dyeing Association, to Berry, R. S., Radian Corporation. November 10, 1983. Response to sodium scrubbing letter.

23. Letter from Vossler, D. A., Union Oil, to Berry, R. S., Radian Corporation. September 7, 1983. Response to sodium scrubbing letter.

24. Letter from Segnar, C. N., Chevron USA, Inc., to Berry, R. S., Radian Corporation. November 1, 1983. Response to sodium scrubbing letter.

25. Letter from Maxwell, G., Cranston Print Works, to Berry, R. S., Radian Corporation. September 1983. Response to sodium scrubbing letter.

26. Letter from Borenstein, M., Neptune/Airpol, to Berry, R. S., Radian Corporation. September 14, 1983. Response to sodium scrubbing letter.

27. Letter from Borenstein, M., Neptune/Airpol, to Berry, R. S., Radian Corporation. June 29, 1983. Response per previous phone conversation with him.

28. Letter from Maddox, J. A., Radian Corporation, to Camponeschi, B., FMC. May 23, 1984. Confirmation of telephone conversation between B. Camponeschi and R. S. Berry (Radian) on June 20, 1983.

29. Letter from Morgester, J. J., California Air Resources Board to Berry, R. S., Radian Corporation. August 9, 1983. Source test data.

30. Memo from Read, B. S., and Jennings, M. S., Radian Corporation, to Larry Jones, EPA. October 8, 1982. FGD Survey, Work Request B.

31. Francis, D. V., ARCO Chemical Company, and R. V. Biolchini, FMC Corporation, Double Alkali Flue Gas Desulfurization Retrofit on an Industrial Cogeneration Facility. Proceedings: Symposium on Flue Gas Desulfurization. Volume 1. (Prepared for the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory and Electric Power Research Institute.) March 1983. pp. 183-200.

32. Letter from Anton, E. C., California Water Resources Control Board to Maddox, J. A., Radian Corporation. June 7, 1984. Confirmation and corrections to telephone call report dated August 26, 1983 between E. C. Anton and R. S. Berry (Radian Corporation).

33. National Academy of Sciences. Water Quality Criteria 1972. (Prepared for the U.S. Environmental Protection Agency.) Washington, DC, 1972. p. 89.

34. Reference 8, Chapter 3.

35. U.S. Environmental Protection Agency. Quality Criteria for Water. Washington, DC. Publication No. EPA-440/9-76-023. 1976. p. 337.

36. Memorandum from Berry, R. S., Radian Corporation, to Industrial Boiler SO_2 Docket. July 20, 1984. Potential Water Quality Impacts of Trace Metals in the Wastewater from Sodium Scrubbers Installed on Coal-Fired Industrial Boilers.

37. Letter from Hereth, M., Radian/Washington, to Berry, R. S., Radian/RTP. October 1983. Projected Promulgation Dates for Wastewater Standards to Point Sources.

38. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and Standards for the Steam Electric Point Source Category. Publication No. EPA No. 440/1-80/029-b. September 1980.

39. Technical Note from Martinez, J. A., Radian Corporation, to the Industrial Boiler SO_2 Docket. April 2, 1984. Emissions from Sodium Scrubbing Wastewater Streams in Sewer Systems. Chapter 1.

40. Letter from Calderwood, C., Kern County APCD, to Maddox, J. A., Radian Corporation. June 4, 1984. Confirmation of information collected in July 25, 1983 telephone conversation between Calderwood and R. S. Berry, Radian Corporation.

41. Letter from Maddox, J. A., Radian Corporation, to Vossler, D., Union Oil Corporation. May 23, 1984. Confirmation of information collected in the September 25, 1983 telephone conversation between Vossler and R. S. Berry (Radian).

42. U.S. Environmental Protection Agency. Background Information Document for Industrial Boilers. EPA Contract No. 68-02-3058. March 25, 1982. pp. 4-69.

43. Weast, R. C. CRC Handbook of Chemistry and Physics. 57th Edition. CRC Press, Cleveland, OH. 1973. pp. B-158 - B-163, B-128.

44. Memo from Martinez, J. A., et al., Radian Corporation, to the Industrial Boiler SO_2 Docket. March 26, 1984. Compilation of SO_2 Emission Data Obtained by EPA Approved Methods from Sodium Scrubbing Systems.

45. Sachtschale, J. R., Santa Fe Energy Company, and J. F. Dydo, FMC Corporation, Operation and Performance of a Double-Alkali Scrubber. Journal of Petroleum Engineering. pp. 2630-2632, 2633-2635. November 1982.

46. Chang, J. C. S. and Dempsey, J. H., Acurex Corporation, and Norm Kaplan, U. S. EPA. Pilot Testing of Limestone Regeneration in Dual Alkali Processes. Proceedings: Symposium on Flue Gas Desulfurization. Volume 1. (Prepared for the U.S. Environmental Protection Agency and Electric Power Research Institute.) March 1983. pp. 201-222.

47. Valencia, J. A., Lunt, R. R., and Ramans, G. J., Industrial Environmental Research Laboratory. Project Summary. Evaluation of the Limestone Dual Alkali Prototype System at Plant Scholz: System Design and Program Plan. (Prepared for the U.S. Environmental Protection Agency.) Research Triangle Park, NC. Publication No. EPA-600/S7-81-141a. September 1981.

48. Durkin, T. H., et al. Operating Experience with a Concentrated Double Alkali Process. (Received as literature from FMC Corporation, May 1983.)

49. Boward, W. L., et al., FMC Corporation. FMC Limestone Double Alkali Process. (Presented at the meeting of the American Institute of Chemical Engineers in Cleveland, OH.) August 30, 1983.

50. LaMantia, C. R., et al, Arthur D. Little. Final Report: Dual Alkali Test and Evaluation Program. Volume III. Prototype Test Program - Plant Scholz. (Prepared for the Industrial Environmental Research Laboratories.) pp. I-4 - I-8.

51. Dickerman, J. R., and Johnson, K. L. (Radian Corporation.) Technology Assessment Report for Industrial Boiler Applications: Flue Gas Desulfurization. (Prepared for the U.S. Environmental Protection Agency.) Research Triangle Park, NC. Publication No. EPA-600/7-79-178i. pp. 2-34 - 2-43, 2-88 - 2-91. November 1979.

52. Letter from Compton, B., Caterpillar Tractor Company, to Martinez, J. A., Radian Corporation. January 5, 1984. Response to Radian questions concerning Caterpillar's dual alkali systems.

53. Tuttle, J., et al., PEDCo Environmental. EPA Industrial Boiler FGD Survey: First Quarter 1979. (Prepared for the U.S. Environmental Protection Agency, Washington, DC.) Publication No. EPA-600/7-79-067b. April 1979.

54. Letter from Maddox, J. A., Radian Corporation, to Baldwin, D. Occidental Chemical Company. May 23, 1984. Confirmation of information obtained in the October 19, 1983 telephone conversation between J. A. Martinez (Radian) and Baldwin.

55. Reference 51, pp. 2-84.

56. Letter from Sachtschale, J. R., Santa Fe Energy Company, to Maddox, J. A., May 31, 1984. Confirmation and corrections to October 18, 1983 telephone conversation between Sachtschale and J. A. Martinez (Radian).

57. Reference 45, pp. 2633-2635.

58. Letter from Maddox, J. A., Radian Corporation, to Friesenhahn, Grissom Air Force Base. May 23, 1984. Confirmation of information collected in the July 5, 1983 telephone conversation between Friesenhahn and R. S. Berry (Radian).

59. Letter from Turner, J. J., St. Regis Paper Company, to Berry, R. S., Radian Corporation. November 1, 1983. Dual alkali information.

60. Letter from Maddox, J. A., Radian Corporation, to Weber, J., Army Corps of Engineers. May 23, 1984. Confirmation of information obtained in the July 5, October 11, and October 12, 1984 telephone conversations between Radian employees and J. Weber.

61. Valencia, J. A., Lunt, R. R., and Ramans, G. J., Industrial Environmental Research Laboratory. Project Summary - Evaluation of the Limestone Dual Alkali Prototype Systems at Plant Scholz: System Design and Program Plan. Publication No. EPA-600/S7-81-141a. September 1981.

62. Behrens, G. P., Radian Corporation. The Current Status of Commercial Flue Gas Desulfurization Systems. (Prepared for the U.S. Environmental Protection Agency, ORD.) Washington, DC. EPA Contract No. 68-02-3171. pp. 205-208. November 1982.

63. Grant, R. J. and Simpson, J. L., CIPS. Full-scale DAFGD Experience at Central Illinois Public Service Company's Newton Station. No date.

64. Van Meter, J. A., and Legatski, J. K., SIGECO, and Durkin, T. H., FMC Corporation. Operating Experience with the FMC Double Alkali Process. (Presented at the EPA Symposium on Flue Gas Desulfurization.) October 29, 1980.

65. Reference 62, pp. 12-15.

66. Letter from Reiners, M., ARCO Chemical, to Maddox, J. A., Radian Corporation. June 6, 1984. Dual Alkali Scrubbers for Industrial Boiler NSPS.

67. U.S. Environmental Protection Agency. Background Information Document for Industrial Boilers, Appendices A-E. (Prepared for OAQPS by Radian Corporation.) March 25, 1982. pp. C-168 - C-186.

68. Memo from Hancock, D. F., Indiana Emissions Sampling Section, to Profit, F. P., Indiana State Board of Health. January 7, 1982. Grissom Air Force Base Emissions Data.

69. Reference 62, p. 41.

70. Corbett, W. E., Hargrove, O. W., Merrill, R. S. (Radian Corporation.) A Summary of the Effects of Important Chemical Variables Upon the Performance of Lime/Limestone Wet Scrubbing Systems. (Prepared for EPRI.) Palo Alto, CA. December 1977. pp. 2-11 - 2-17.

71. Reference 62, pp. 51-54.

72. Wen, C. Y. and Fan, L. S. Absorption of Sulfur Dioxide in Spray Column and Turbulent Contacting Absorbers. Final Report. Publication No. EPA-600/2-75-023. Morgantown, WV. West Virginia University. August 1975.

73. Knight, R., Gorden and Steve L. Pernick, "Duquesne Light Company, Elrama and Phillips Power Stations Lime Scrubbing Facilities", in Proceedings, Symposium on Flue Gas Desulfurization, New Orleans, March 1976, Volume 1, Research Triangle Park, NC, 1976, pp. 205 ff.

74. Borgwardt, R. H., Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant, Progress Report No. 16. Research Triangle Park, NC. Undated.

75. Cronkright, Walter A. and William J. Leddy, "Improving Mass Transfer Characteristics of Limestone Slurries by Use of Magnesium Sulfate", Environmental Science & Technology. 10(6), 1976. pp. 659-672.

76. Reference 51, pp. 2-34 - 2-43.

77. Saleem, A. (Chemico Air Pollution Control Corp.) Spray Tower: The Workhorse of Flue Gas Desulfurization. Power Magazine. 124 (10): 73-77. October 1980.

78. Reference 62, p. 42.

79. Clarke, et al. Evaluation of the Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process on an Industrial Boiler. EPA Contract 68-02-3173. Project Summary. Research Triangle Park, NC. July 1981.

80. Letter from Haines, R. P., RANGB, to Maddox, J. A., Radian Corporation. June 1, 1984. Verification of telephone call information - September 19, 1983.

81. Letter from Maddox, J. A., Radian Corporation, to Saleem, A., General Electric Company. May 23, 1984. Confirmation of information collected in June 9, 1983 telephone conversation between Saleem and R. S. Berry (Radian) about wet FGD developments.

82. Letter from Maddox, J. A., Radian Corporation, to Diomigo, A., Thyssen-CEA. May 23, 1984. Confirmation of information collected in June 9, 1983 telephone conversation between Saleem and R. S. Berry (Radian) about wet FGD developments.

83. Letter from Byrne, R. E., Research Cottrell, to Berry, R. S., Radian Corporation. August 16, 1983. Wet and dry FGD developments.

84. Reference 62, p. 5-15.

85. U.S. Environmental Protection Agency. The Effect of Flue Gas Desulfurization Availability on Electric Utilities. Volume II. Technical Report. Publication No. EPA-600/7-78-031b. March 1978.

86. Reference 51, pp. 2-81 - 2-91.

87. Doctor, R. D. Utility Flue Gas Desulfurization: Innovations and System Availability. (Prepared for U.S. Department of Energy.) March 1982.

88. Reference 62, p. 65.

89. Wange, S. C. and Burbank, D. A. (Bechtel National, Inc.) Adipic Acid-Enhanced Lime and Limestone Testing at the EPA Alkali Scrubbing Test Facility. Volume 1. (Prepared for the U.S. Environmental Protection Agency). Washington, DC. p. 274. July 1981.

90. Clarke, P. A., et al. (PEDCo.) The Adipic Acid-Enhanced Flue Gas Desulfurization Process for Industrial Boilers. Volume I. Field Test Results. (Prepared for U.S. Environmental Protection Agency.) Research Triangle Park, NC. November 1982. Chapter 3.

91. Kelly, W. E. et al. U.S. Environmental Protection Agency. Air Pollution Emission Test. Third Interim Report: Continuous Sulfur Dioxide Monitoring at Steam Generators. Volume I. Summary of Results. EMB Report No. 77-SPP-23C. p. 1. March 1979.

92. Melia, M. T., et al. PEDCo Environmental, Inc. Utility FGD Survey July 1982 - March 1983. Volume II. Design and Performance Data for Operational FGD Systems, Part I. EPRI Contract No. RP982-32/EPA Contract No. 68-02-3173. pp. 442-454.

93. Reference 62, p. 189.

94. Hargrove, O. W., et al. Full Scale Utility FGD System Adipic Acid Demonstration Program. Publication No. EPA-600/7-83-035. October 1983.

95. Letter from Carlton, J. C., Pfizer Corporation, to Berry, R. S., Radian Corporation. September 26, 1983. Response to lime scrubbing questions.

96. Reference 62, pp. 78-79.

97. Letter from Stowe, D. H., Dravo Lime Corporation, to Maddox, J. A., Radian Corporation. June 8, 1984. Status of the Thiosorbic process.

98. Henzel, D. S. and D. H. Stowe, Dravo Lime Corporation. A Proven Reagent for High Sulfur Coal Flue Gas Desulfurization. (Prepared for the 7th Symposium on Flue Gas Desulfurization. Hollywood, FL. May 17-20, 1982.)

99. Reference 43, p. B-128.

100. Letter from Maddox, J. A., Radian Corporation, to Anderson, Carborundum Abrasives Company. June 5, 1984. Verification of information collected in July 12, 1983 and May 30, 1984 telephone conversations.

101. Letter from Barker, J. E., Armco Steel, to Maddox, J. A., Radian Corporation. June 8, 1984. Verification of information collected in the July 12, 1983 telephone conversation between Barker and R. S. Berry (Radian).

102. Downs, W., W. J. Sanders and C. E. Miller. Control of SO_2 Emissions by Dry Scrubbing. (Presented at the American Power Conference. Chicago, Illinois. April 21-23, 1980.)

103. Getler, J. L., H. L. Shelton, and D. A. Furlong. Modeling the Spray Dryer Absorption Process for SO_2 Removal. Journal of the Air Pollution Control Association. 29(12): 1270-1274. December 1979.

104. Kelly, M. E. and M. A. Palazzolo. (Radian Corporation.) Status of Dry SO_2 Control Systems: Fall 1982. (Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C.) EPA Publication No. 600/7-83-041. August 1983. pp. 2-28, 12-13, 54-58, 71.

105. Palazzolo, M. A. and M. A. Baviello (Radian Corporation). Status of Dry SO_2 Control Systems: Fall, 1983. pp. 7-38, 40-42, 78-80.

106. Reference 105, pp. 88-104.

107. Stevens, N. J., et al. Dry SO_2 Scrubbing Test Program. Draft report. (Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C.). EPA Contract No. 68-02-3190. May 1981. p. 48.

108. Blythe, G. M. Field Evaluation of a Utility Dry Scrubbing System. (Presented at the 1983 EPA/EPRI Symposium on Flue Gas Desulfurization. New Orleans, Louisiana. November 1-4, 1983.)

109. Reference 42, pp. 4-85 - 4-90.

110. Reference 105, pp. 78-80.

111. Reference 105, pp. 32-38.

112. Reference 105, pp. 40-42.

113. Reference 105, pp. 7-23.

114. Memo from Jones, G. D., Radian Corporation, to Sedman, C., EPA/ISB. July 30, 1984. Evaluation of Reliability and Availability of Industrial Spray Drying Systems.

115. Mudgett, J. S., R. S. Sadowski, W. W. West, and M. Mutsakis. Dry Flue Gas Desulfurization System in an Industrial Plant. In: Proceedings of the American Power Conference. Volume 44. Chicago, 1982. pp. 1003-1012.

116. Crowe, R. B. First-year Operational Experience Celanese Fibers Company Coal-Fired Boiler Using a Dry Flue Gas Cleaning System. (Presented at the 74th Annual Meeting of the Air Pollution Control Association. Philadelphia, Pennsylvania. June 21-26, 1981. Paper #81-35.2.)

117. Farber, Paul S. Start-up and Performance of a High Sulfur Dry Scrubber System. (Presented at the 75th Annual Meeting of the Air Pollution Control Association. New Orleans, Louisiana. June 20-25, 1982. Paper #82-40.5).

118. Burnett, T. A. and K. D. Anderson. Technical Review of Dry FGD Systems and Economic Evaluation of Spray Dryer FGD Systems. (Prepared for U.S. Environmental Protection Agency and Tennessee Valley Authority, Research Triangle Park, N.C.) EPA Publication No. 600/7-81-014, TVA Publication No. EDT-127, NTIS No. PB 81-206476. February 1981.

119. Apple, C. and M. E. Kelly. Mechanisms of Dry SO_2 Control Processes. (Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C.) Publication No. EPA-600/7-82-026. April 1982. pp. 61-63, 80-100.

120. Yeh, J. T., R. J. Demski and J. I. Joubert. Control of SO_2 Emissions by Dry Sorbent Injection. In: Flue Gas Desulfurization, ACS Symposium Series 188. Washington, DC. American Chemical Society. 1982. p. 350.

121. Reference 119, pp. 80-87.

122. Muzio, L. J., et al. Demonstration of SO_2 Removal on a Coal-Fired Boiler by Injection of Dry Sodium Compounds. In Proceedings: Symposium on Flue Gas Desulfurization - Volume Z. Palo Alto, Electric Power Research Institute. March 1983. pp. 628-649.

123. Reference 104, pp. 54-58.

124. Davis, W. T. and T. C. Keener. Chemical Kinetics Studies on Dry Sorbents - Literature Review. (Prepared for U.S. Department of Energy, Grand Forks, North Dakota.) Publication No. DOE/FC/10184-2. August 10, 1980. pp. 42-56.

125. Naulty, D. J. Economics of Dry FGD Sorbent Injection. (Presented at the 76th Annual Meeting of the Air Pollution Control Association. Atlanta, Georgia. June 19-24, 1983. Paper #83-38.6.) 23 p.

126. Reference 119, pp. 80-100.

127. Muzio, L. J., et al. Dry SO_2 - Particulate Removal for Coal-Fired Boilers. Volume 1. Demonstration of SO_2 Removal on a 22-MW Coal-Fired Utility Boiler by Dry Injection of Nahcolite. (Prepared for Electric Power Research Institute, Palo Alto, CA.) EPRI CS-2894. March 1983.

128. Reference 119, pp. 61-63.

129. U.S. Environmental Protection Agency. Evaluation of Dry Sorbents and Fabric Filtration for FGD. Research Triangle Park, N.C. Publication No. EPA-600/7-79-005. January 1979. p. 60-62.

130. Reference 105, pp. 29-30.

131. Reference 42, pp. 4-160.

132. Solution Mining of Nahcolite (natural sodium bicarbonate) may begin by 1986. Chemical Engineering. 90(12):20. June 13, 1983.

133. Shah, N. D. (Multi Mineral Corporation.) Dry Scrubbing of SO_2. Chemical Engineering Progress. 78(6):73-77. June 1982.

134. Reference 129, p. 2.

135. Reference 104, pp. 12 and 13.

136. Trexler, E. C. DOE's Electron Beam Irradiation Developmental Program. In Proceedings: Symposium on Dry Flue Gas Desulfurization. Palo Alto, Electric Power Research Institute. March 1983. p. 359.

137. Reference 105, pp. 30-31.

138. Reference 104, p. 71.

139. Menegozzi, L. and P. L. Feldman. Removal of NO_x, SO_2 by Electron Beam Irradiation; A Phenomenological Model. (Presented at the 74th Annual Meeting of the Air Pollution Control Association. Philadelphia, Pennsylvania. June 21-26, 1981.) 19 p.

140. Reference 42, pp. 4-160.

3.0 COMBUSTION MODIFICATION CONTROL APPROACHES

Approaches for reducing SO_2 and NO_x emissions from coal-fired industrial boilers through combustion modification are assessed in this section. Control methods assessed include fluidized bed combustion combustion (FBC), limestone injection in multi-stage burners (LIMB) and combustion of coal/limestone pellets. Information concerning the reliability and economics of these technologies is generally unavailable.

3.1 FLUIDIZED BED COMBUSTION

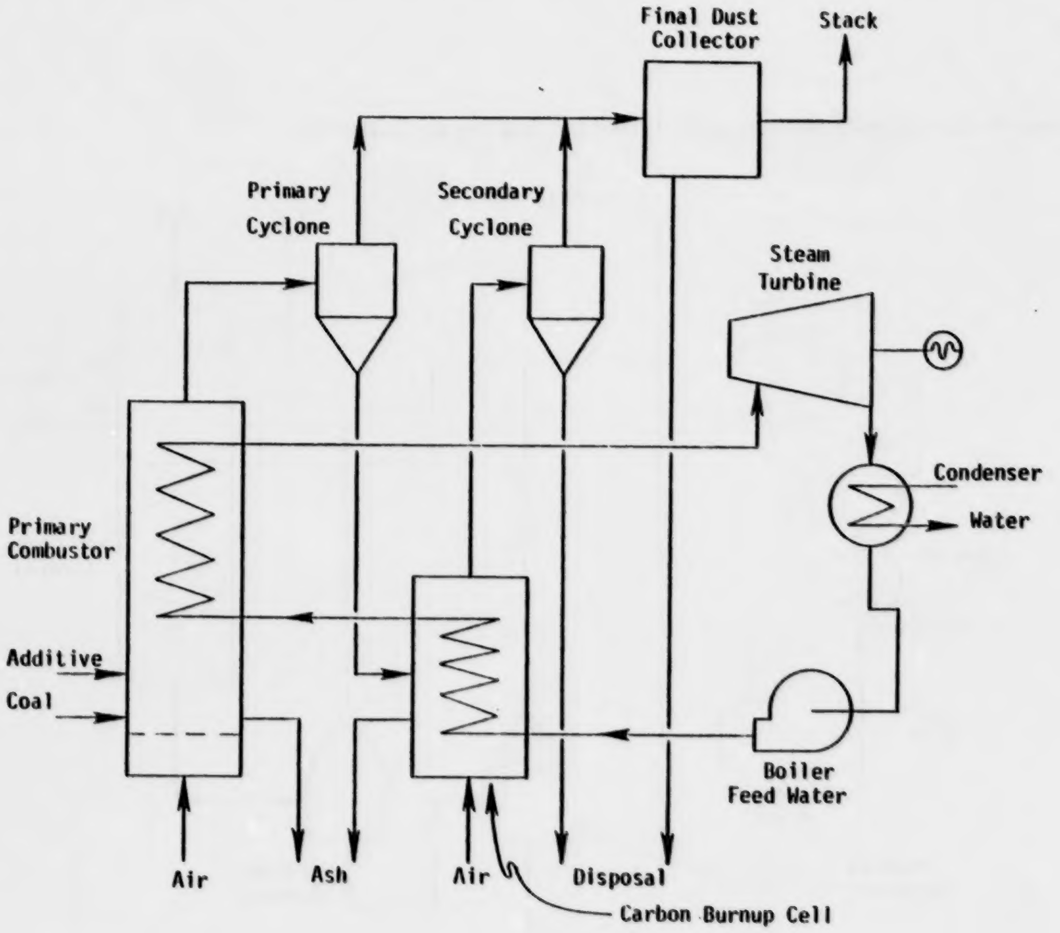
Fluidized bed combustion (FBC) is being investigated as an alternative to conventional combustion techniques for industrial coal-fired boiler applications (e.g., stoker-fired, pulverized-coal, etc). Fluidized bed boilers (FBC) offer potential advantages in both boiler design and emissions control. The fluidized bed promotes higher heat transfer rates which results in reduced heat transfer surface requirements. The fluidized bed also operates at a lower temperature which produces lower NO_x emissions. Addition of limestone to the bed allows sulfur to be captured in-situ which eliminates the need for an FGD system to control SO_2 emissions. Also, the ability of an FBC unit to burn a wide variety of fuels provides fuel flexibility to users. The primary motivation for development of FBC technology in Europe and Asia has been fuel flexibility; the technology is being developed in the U.S. to comply with environmental regulations and for retrofit applications.

During the past decade, a number of development programs have been sponsored by both governmental and private organizations to quantify the advantages of FBC technology and to evaluate its feasibility in commercial applications. Issues of concern with respect to FBC commercialization included performance, cost, reliability, and environmental impact. The earlier development programs did not demonstrate a clear-cut advantage for FBC compared to conventional boilers. However, more recently, industrial-sized FBC have become available commercially in the United States; over 80 FBC installations are operating or scheduled for start-up prior to 1985.[1] As a part of the recent commercialization activity, several new design concepts have been introduced. These new design concepts have produced configurations which include: 1) the use of recycle for traditional dense-bed FBC systems, 2) circulating beds, and 3) staged-beds.

The first set of SO_2 emissions data for industrial FBC units burning coal were collected at the Georgetown University (GU) facility. This unit was operated to meet an emissions limit of 0.78 lb $SO_2/10^6$ Btu, corresponding to a median of 85 percent removal on a 3 percent sulfur coal. Results from the GU unit showed a high degree of emissions variability due to design problems and operating procedures; the performance results are probably a conservative estimate of what a well-designed, well-operated FBC dense-bed system can achieve. Emissions data have also been collected on the Tennessee Valley Authority's (TVA's) 20 MW_e dense bed FBC pilot plant designed for utility applications. This system demonstrated 87 percent SO_2 removal with no solids recycle and 98 percent removal with solids recycle. These results are not directly translatable to an industrial FBC system, however, due to the large freeboard height associated with the TVA plant; greater freeboard height facilitates SO_2 emissions reduction. Emissions from advanced bed design show mixed results: 82-83 percent SO_2 removal from two-stage beds and 90-96 percent removal from circulating bed facilities.

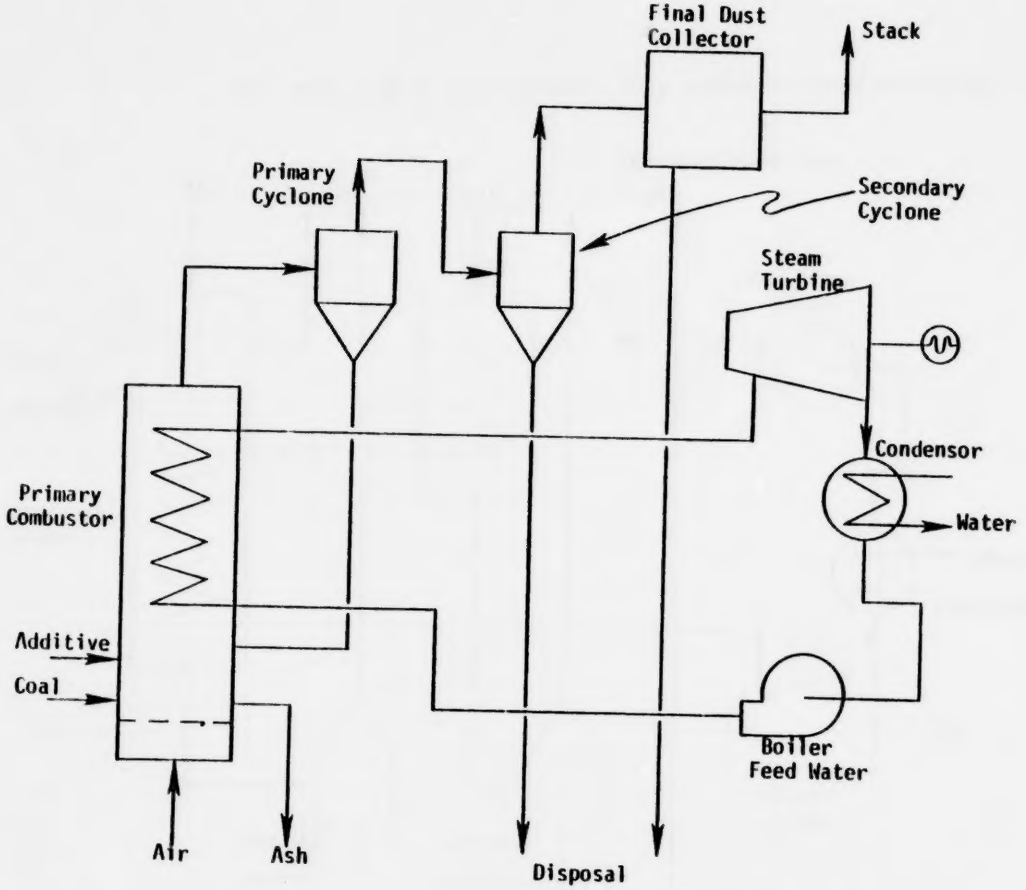
3.1.1. Process Description

Simplified schematic diagrams of several traditional dense-bed FBC system designs are presented in Figure 3.1-1. While the figure illustrates configurations generating electrical power, these same systems can produce steam for industrial applications. An atmospheric fluidized bed combustion (AFBC) boiler equipped with a separate carbon-burnup cell is presented in Figure 3.1-1a. This design concept has been abandoned in favor of the recycle configuration presented in Figure 3.1-1b where elutriated particles from the bed are collected by a cyclone and recirculated back to the bed. In addition to the cyclones, downstream fabric filters or ESPs are necessary to further reduce flue gas particulate emissions. A pressurized fluidized bed combustion (PFBC) system operating in the combined-cycle mode is presented in Figure 3.1-1c. Since it appears that AFBC boilers will dominate the industrial FBC market in the near future only AFBC designs are considered in the following sections.



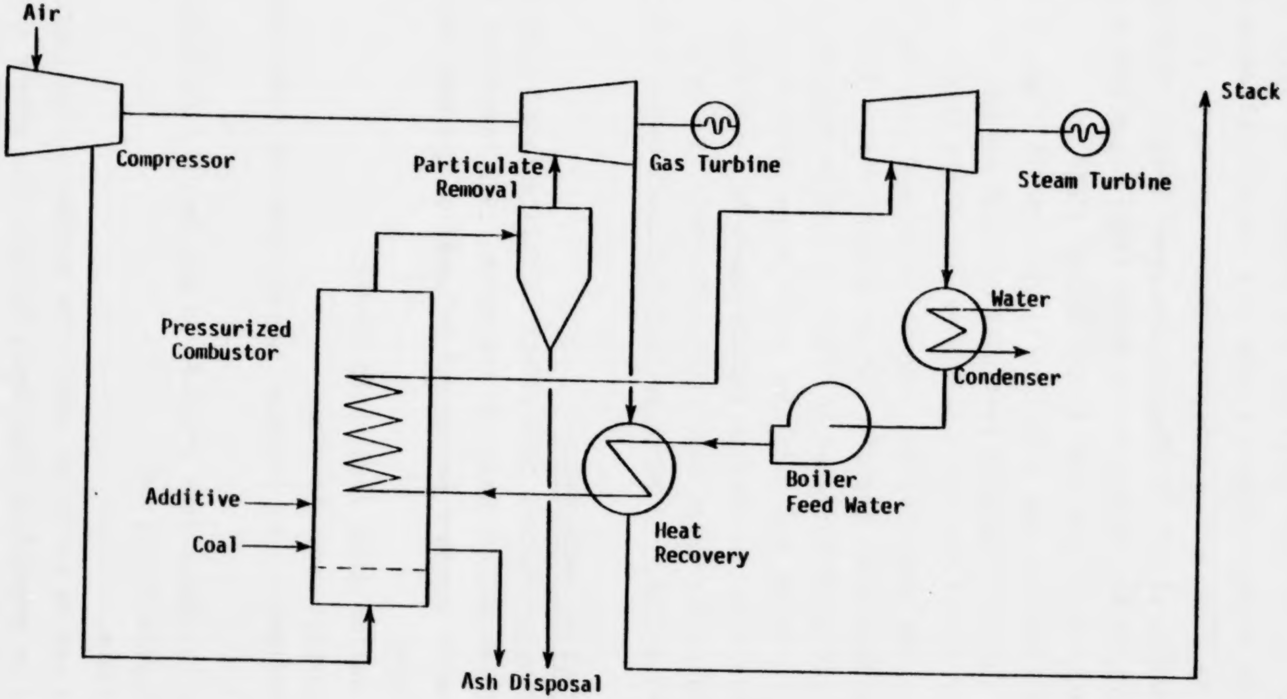
(a) Water-Cooled AFBC Combustor with Separate Carbon-Burnup Cell

Figure 3.1-1. Schematics of Traditional Dense-Bed FBC Power - Generation Systems[2]



(b) Water-Cooled AFBC Combustor with Recycle from Primary Cyclone

Figure 3.1-1 (con't.)



(c) PFBC Water-Cooled Combustor/Combined-Cycle Plant

Figure 3.1.1 (con't.)

Two newer AFBC design configurations are presented in Figure 3.1-2. The two-stage system shown in Figure 3.1-2a is a traditional dense-bed FBC system where coal is fired with a substoichiometric amount of air in the lower stage and additional air is added in the upper stage. This approach decreases the amount of NO_x formed in the first stage but allows acceptable combustion efficiency to be achieved in the second stage.

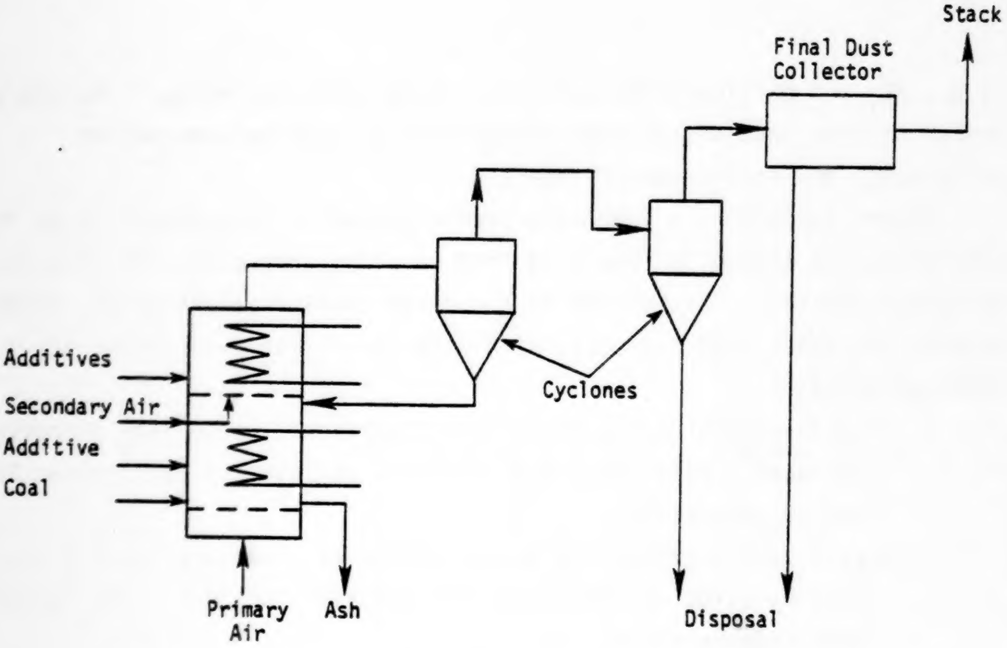
A circulating fluidized bed (CFBC) is illustrated in Figure 3.1-2b. The CFBC utilizes smaller limestone particles and high combustion-air velocities to carry all of the solid particles out of the combustion reactor in a dilute phase. The particles are then collected and returned to the combustor. The required heat transfer can be accomplished either in the dilute gas phase section as pictured in Figure 3.1-2b or externally by heat exchange with the collected hot particles prior to reinjection into the combustor. Potential CFBC advantages include lower NO_x emissions, improved limestone utilization, increased combustion efficiency, a simpler coal/limestone feed system, and improved load-following capability.[2]

3.1.2. Factors Affecting Performance

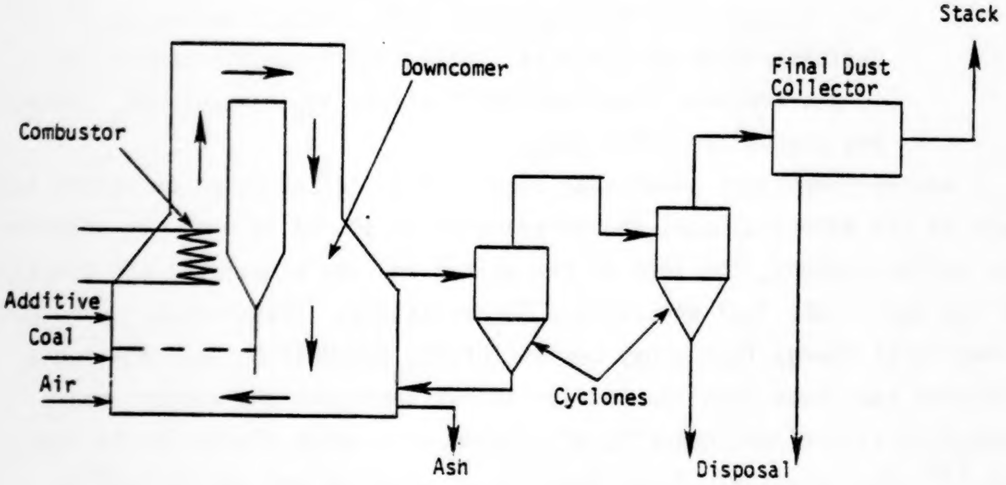
The following major factors that affect sulfur capture in the AFBC boiler were identified and discussed in the March, 1982 Industrial Boiler New Source Performance Standard Background Information Document (BID).[3] These factors include:

- calcium-to-sulfur molar feed ratio (Ca/S);
- limestone sorbent particle size;
- gas phase residence time (related to bed depth and superficial gas velocity);
- solid phase residence time (related to bed depth, feed mechanism, and solids recycle rate); and
- bed temperature.

These factors can be varied to obtain the optimum sulfur capture. However, it should be emphasized that these factors also affect other important performance variables including boiler operation (e.g., combustion efficiency, boiler efficiency, etc.) and control of other flue gas emissions



(a) Water-Cooled AFBC Unit with Two-Staged Combustor



(b) Water-Cooled AFBC Unit with Circulating Bed

Figure 3.1-2. Schematics of Two-Stage and Circulating-Bed AFBC Power-Generation Systems[2]

(e.g., NO_x and particulates) and solid waste characteristics. Therefore, a number of important design compromises must be made between boiler performance and environmental impact.

Recent designs have been more sophisticated in response to needs for optimizing the tradeoffs resulting from coupling combustion and in-situ emissions control. The effects of the newer configurations on SO_2 emissions control and associated tradeoffs with other performance variables are itemized below:

- Recycle of elutriated fines from traditional dense beds improves combustion efficiency and limestone utilization and reduces SO_2 and NO_x emissions.
- Staged beds overcome the design tradeoffs associated with a one-bed unit by allowing combustion and emissions control to be optimized more independently.
- Circulating beds allow the units to be operated at different conditions than traditional dense-beds (e.g., limestone size, superficial velocity, residence time, mixing) and allow performance to be optimized under more favorable conditions (e.g., improved limestone utilization, SO_2 control, NO_x control, and combustion efficiency).

Another important point that should be discussed based on recent test data is the effect of coal characteristics on SO_2 emissions. In addition to the sulfur content, the form of the sulfur and the alkalinity and quantity of the ash in the fuel will affect SO_2 emissions. Tests conducted by DOE's Grand Forks Energy Technology Center (GFETC) and METC on low-rank fuels indicate that some lignites and low-sulfur subbituminous western coals contain a significant quantity of calcium and sodium alkalinity in their ash.[4,5] The relatively large quantity of alkaline ash and low sulfur content combine to provide significant sulfur capture. In tests conducted with a Beulah, North Dakota lignite, the inherent alkali-to-sulfur ratio ranged between 0.5 and 1.2 for low-sodium and high sodium lignite ashes respectively. To achieve 90 percent sulfur capture, the low-sodium Beulah lignite required only enough limestone to be added to produce an external alkali-to-sulfur ratio of 0.75. Furthermore, the high-sodium lignite contained sufficient inherent alkalinity in the ash to achieve 90 percent sulfur capture without the addition of any limestone. Recent tests with Texas lignites indicate that ash and sulfur characteristics other than alkali-to-sulfur ratio also affect sulfur capture efficiency (i.e., silica-to-sodium ratio).

Although sodium in the fuel contributes to improved sulfur capture, it also increases the agglomerating tendency of the fuel. High sodium levels in lignite lower the melting point of the ash and cause the particles in the bed to stick together. Agglomeration can cause a number of operating problems including loss of fluidization, loss of bed temperature uniformity, plugging of recycle lines, reduced combustion efficiency, and decreased heat transfer rate.

3.1.3. Applicability to Industrial Boilers. Only a handful of vendors offered industrial AFBC boilers in the U.S. in 1979 on a commercial basis. Today, approximately 40 manufacturers offer AFBC boilers capable of producing from 10,000 to 600,000 lb/hr of steam at conditions comparable to conventional boilers. Many are offering guaranteed systems for a wide variety of applications.[1]

The price and availability of premium fuels as well as long-term environmental concerns have made AFBC a viable option compared to stoker-fired and pulverized-coal fired units. SO_2 and NO_x emissions control achieved within the combustion chamber can eliminate the need for scrubbers, lower sulfur coal purchases, or elaborate combustion modifications. The fuel flexibility provided by FBC technology allows a wide range of solid fuels with varying ash and moisture contents to be successfully burned within a single boiler. In the U.S., AFBC boilers are generally cost-competitive with conventional industrial boilers equipped with scrubbers.[1]

The number of AFBC boilers operating throughout the world has increased dramatically in recent years. In China alone, over 2,000 AFBC boilers combust low grade fuels containing up to 70 percent ash. The AFBC units are used because of their ability to combust the low grade fuels. In general, limestone is not added for SO_2 removal in China. These boilers are generally small and are frequently located in remote areas.[6]

Outside of China, over 130 industrial-sized AFBC boilers are operating or planned for operation in the near future. These boilers are designed to represent a wide range of requirements such as size, fuel type, and steam conditions for a variety of industrial applications. Their sizes range from 10,000 to 600,000 lb/hr of steam. Over 22 different types of fuels are planned for use including low rank fossil fuels (lignite and peat) and waste from process industry, agricultural, and municipal sources. Steam pressures in excess of 2,500 psi are generated. These installations also represent all of the major types of design configurations including the more recently introduced staged and circulating bed designs.[1]

Of the over 130 units outside China, 80 units are located in the United States. Excluding AFBC boilers that are test, demonstration, or uncompleted units, only eight AFBC boilers in the United States burn coal. Information describing five of the coal-fired AFBC units is summarized in Table 3.1-1. This type of information is not currently available for the remaining three units. Comparisons of the five units presented in Table 3.1-1 indicate the variability in design and operating conditions for these initial commercial installations.

Despite the availability of commercial units and the increasing number of installations, some potential users of AFBC boilers remain skeptical of the overall technical and economic advantage of this relatively new approach for steam and power generation. To reduce the reluctance of potential users, the technology must continue to be improved and optimized to address continuing issues associated with unit subsystems. Then, the technology must be adequately demonstrated in various industrial applications to prove its flexibility in meeting specific process requirements.

TABLE 3.1-1. PARTIAL SUMMARY OF COAL-FIRED INDUSTRIAL AFBC BOILERS IN THE U. S.

	Plant A	Plant B	Plant C	Plant D[g]	Plant E
Construction	Field	Field	Field	Field	Package
Bed Configuration	Circulating	Circulating	Conventional Bubbling Bed	Conventional Bubbling Bed	Conventional Bubbling Bed
Features					
Solids Recycle	Yes[a]	Yes	Yes	No	Yes[i]
Staged Combustion Air	Yes	Yes	No	No	No
Limestone for SO_2 Removal	Yes	Yes	Yes	No[d]	No
Recycle Ratio	NA[h]	Not Determined	Not Determined	NA	NA
Primary/Stoichiometric Air Ratio	0.6	Confidential	NA	NA	NA
Ca/S Ratio	3.5	3 or 4	2	NA	NA
Percent SO_2 Removal	90	Not Determined	Not Determined	NA	NA
Fuel					
Type	Coal	Coal	Coal	Coal	Coal
Heating Value (HHV), Btu/lb	7,937	10,000	Not Available	Not Available	12,085
Sulfur Content, %	0.5[b]	0.6	0.8/1.5[f]	1.0	3
Alternate Fuels	Petroleum Coke	Coke[c]	-[e]	None	None
Boiler Efficiency, %	72	Not Determined	Not Determined	Not Available	83.5
Availability, %	85[j]	Not Determined	Not Determined	Not Available	Not Available
CEM[k] Equipment					
SO_2	Yes	Yes	Yes	No	No
NO_x	Yes	Yes	Yes	No	No
CO	Yes	No	Yes	No	No
CO_2	Yes	No	No	No	No
Particulates	Yes	Yes	Yes	No	No
Recurring Problems	None	NA	NA	NA	Water Tube & Wall Erosion
Status	Operational, Dec, 1981 Compliance testing Completed July 1983	Operational July, 1983	Operational August, 1983	Operational August, 1981 Currently operating with cost-cutting measures.	Operational April, 1980 Problems with erosion of water tubes and walls.

[a] Additional solids recycle, beyond that provided by the circulating bed, is available but not being used.

[b] Average total fuel stream contains approximately 2 percent sulfur. Petroleum coke contains approximately 7 percent sulfur and has a higher heating value of 14,943 Btu/lb.

[c] After the unit comes on-line, oil-impregnated diatamaeous earth will be tested for use as a fuel.

[d] Limestone used only for bed material due to liberal emission requirements and as a cost-cutting measure.

[e] The decision to use or not to use alternate fuels has not been made.

[f] Two different coals with different sulfur contents will be used depending on economics.

[g] Information gathered from manufacturer at suggestion of operator.

[h] Not applicable.

[i] Solids recycle incorporated originally, but presently inoperable due to mechanical problems.

[j] Does not include down time resulting from electrical power outrages.

[k] Continuou[illegible]ission monitoring.

3.1.4. Development Status. Research and development (R&D) began in England in the 1960's to develop FBC technology as an improved method for burning coal. In the United States, a significant R&D effort was conducted during the 1970's. Much of the work was sponsored by the U.S. Department of Energy (DOE). Recently, the DOE's overall mission has shifted from large, demonstration projects to bench-scale, high-risk, advanced concept research.[7] Since DOE regards conventional AFBC technology as commercialized, further commercial development of AFBC technology has become the responsibility of the private sector. DOE has halted its participation in large-scale demonstration programs at Georgetown University, Great Lakes Naval Station, Shamokin Area Industrial Corporation, and United Shoe Manufacturing Corporation. As an example of DOE's shift of emphasis toward more advanced technology, the goal of DOE Morgantown Energy Technology Center's (METC) advanced AFBC projects is to achieve 90 percent sulfur capture on high sulfur coal with a calcium-to-sulfur (Ca/S) molar ratio of 1.5 or less.[8]

The Electric Power Research Institute (EPRI) is sponsoring programs aimed at developing FBC technology for utility applications. EPRI is sponsoring testing at the Babcock and Wilcox (B&W) 6' x 6' unit at Alliance, Ohio. EPRI is supporting a test program initiated in 1982 at a 20 MW_e AFBC pilot plant operated by the Tennessee Valley Authority (TVA) at their Shawnee Generating Station. While these programs are directed toward utility applications, many of the technical issues addressed are directly applicable to industrial boiler facilities.

Currently, 80 industrial FBC installations are operating or scheduled for start-up in the United States prior to 1985. Only nine of these installations are designed for coal combustion. Most of the other units will use wood, oil, natural gas, process gas, or process wastes as a fuel source.

3.1.5. Emission Test Data

In the past, SO_2 emissions data have been collected primarily from small scale test equipment operating over a wide range of conditions. More recently, SO_2 emissions data have been collected at large commercial scale operations. A summary of available SO_2 removal data for the various AFBC configurations is presented in Table 3.1-2.

One of the first sources of continuous emissions data from a commercial scale facility was the dense-bed AFBC unit located at Georgetown University (GU).[9] At GU, the unit was operated to meet the District of Columbia emission limit of 0.78 lb $SO_2/10^6$ Btu. The median SO_2 removal efficiency has been about 85 percent with 3 percent sulfur coals at Ca/S ratios between 4 to 6. Actual SO_2 emissions varied over a broad range due principally to the coal sulfur variability. During periods when the coal was sampled on an hourly basis, SO_2 removal efficiency ranged from 80 to 90 percent at Ca/S ratios of 4 to 7. However, significant design and operating problems have been encountered at GU which have resulted in higher Ca/S ratios than originally anticipated. The Ca/S ratios observed at GU are probably higher than would be required if the system design and operation were optimized.

The effect of solids recycle on dense bed performance is dramatically illustrated at TVA's 20 MWe pilot unit where removal at a Ca/S of 3.0 increased from 87 percent with no recycle to 98 percent with a recycle ratio of 1.5.[10] EPRI's target for sulfur capture is to achieve 90 percent removal at a Ca/S of 2.0. This target is predicted based on an evaluation of test performance results.

The TVA 20 MW_e pilot plant design provides greater sulfur capture efficiency than the older unit at Georgetown University. It should be noted, however, that the outstanding SO_2 removal performance of the TVA 20 MW_e pilot plant operating with solids recycle may be aided by the higher freeboard of this unit. Freeboard height at the TVA unit is over 20 feet compared to about 10 feet for a typical industrial fluidized bed boiler. The higher freeboard allows more time for SO_2 capture by entrained sorbent, effectively increasing the in-bed gas residence time.

TABLE 3.1-2. SUMMARY OF SO_2 EMISSIONS DATA FOR VARIOUS AFBC CONFIGURATIONS

AFBC Configuration	Capacity lb steam/hr	Coal Type (Percent Sulfur)	Combustion Temperature	Ca/S Ratio	Type of SO_2 Emissions Monitoring/Length of Monitoring Period	SO_2 Removal
Conventional Bubbling Bed						
Georgetown University[a]	100,000	Eastern bituminous (1.5 - 2.0%S)	1550°F	3-6	CEM/23 days	75 - 95%
TVA 20 MW(e)						
- no recycle	150,000	Eastern bituminous (3.7%S)	1550°F	3.0	CEM/ND	87%
- Recycle ratio[b] = 1.5				3.0		98%
Staged Bed						
Wormser - United Shoe Manufacturing Corp	2,500[c]	Eastern bituminous (1.5%S)	1800°F[d] 1550°F[e]	3.0	CEM/1000 hr	83%
Wormser -- Iowa Beef Processors	70,000	Midwestern bituminous (4.2%S)	1750°F[d] 1550°F[e]	3.0	CEM/ 10 hr	82%
Circulating Bed						
Lurgi	ND	Eastern bituminous (3%S)[c]	1560°F	1.5	ND/ND	90%
Battelle MS-FBC	55,000	Various (2%S)[f]	1650°F	3.0	CEM/55 days	95%

ND = Data not available

CEM = Continuous emissions monitoring

[a] Solids are recycled but at an unknown rate.

[b] Recycle ratio is defined as the ratio of the recycle mass rate to the coal feed mass rate.

[c] Approximate.

[d] Combustion bed.

[e] Desulfurization bed.

[f] Fuels include a 1.5% sulfur Texas coal and a 7.1% petroleum coke, with an average feed sulfur content of approximately 2.0%.

The capability of staged combustion is also illustrated in Table 3.1-2. Wormer's staged combustion concept achieved approximately 80 percent SO_2 removal at a Ca/S molar ratio of 3.0 at two different installations, one firing high sulfur coal and the other firing low sulfur coal.[11,12]

The performance of two circulating bed design concepts is also summarized in Table 3.1-2. The Lurgi circulating bed data demonstrates a significant improvement in limestone utilization and removal efficiencies over the other design configurations. Lurgi's staged circulating bed achieved 90 percent sulfur capture at a Ca/S ratio of 1.5 while operated at full capacity with excess air levels of 15 to 20 percent.[13] Battelle's Multi-Solids FBC unit obtained 95 percent removal at a Ca/S ratio of 4.5.[14]

The data presented in Table 3.1-2 serve to compare the trends provided by the newer configurations with respect to SO_2 emissions. More data are necessary to provide a direct comparison of optimum SO_2 control for configurations at comparable design and operating conditions.

3.2 LIMB

LIMB is a developing technology which is capable of achieving simultaneous reductions in sulfur oxides (SO_x) and nitrogen oxides (NO_x) emissions from pulverized coal boilers. The term "LIMB" is short for Limestone Injection Multistaged Burners. This technology is based on the use of low NO_x combustion techniques in combination with dry limestone injection into the furnace for simultaneous SO_x control.

The goal of ongoing LIMB R&D is to develop a technology which can substantially reduce SO_x and NO_x emissions for a capital investment of \$30-40/kW -- about 1/5 of the cost of conventional flue gas desulfurization (FGD) systems. For new coal-fired boiler applications the goal is to achieve SO_2 removals of 70 percent with simultaneous NO_x emission levels of 86-130 ng/J (0.2-0.3 lb/million Btu).

Since LIMB techniques are only now beginning to be evaluated in commercial-scale combustion equipment, it will be several years before any meaningful data on the long term costs, benefits and/or problems associated with this technology are known. Initial test results in small scale equipment have been promising, however.

3.2.1 Process Description

In the LIMB process, dry, finely ground limestone is injected into the furnace either through the burners, or through separate injection ports installed in the furnace wall.

If limestone is used as the alkaline reagent in a LIMB system, the following are among the key reactions which will occur:

Calcination -

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (3.2.2\text{-}1)$$

Reaction with reduced sulfur species in fuel-rich zones -

$$CaO + H_2S \rightarrow CaS + H_2O \qquad (3.2.2\text{-}2)$$

Sulfation -

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (3.2.2\text{-}3)$$

Product solids, along with any unreacted limestone are entrained in the flue gas and collected along with fly ash in a downstream particulate control device such as an electrostatic precipitator or fabric filter.

In order for LIMB to be effective in controlling SO_2 emissions, the alkaline reagent must be injected under conditions which are favorable for sulfur capture via Equations 3.2.2-2 and 3.2.2-3. This requires the integration of limestone injection control for SO_2 with the use of low NO_x combustion techniques. The two techniques presently under development for use in LIMB technology are the distributed mixing burner (DMB) for wall-fired pulverized coal boilers and the fuel rich fireball for tangentially-fired boilers.

The distributed mixing burner is shown conceptually in Figure 3.2-1. Coal and primary combustion air are injected through a central fuel injector. The coal begins to burn in a very fuel-rich zone. Secondary air admitted through two concentric throats gradually mixes with the primary reactants. The final mixture in the burner zone is still fuel-rich, having about 70 percent of the air required for complete combustion. These fuel-rich conditions minimize the formation of fuel NO_x by promoting maximum conversion of the chemically-bound nitrogen in the coal to molecular nitrogen. The balance of the air necessary for complete combustion is admitted through tertiary ports spaced around the burner periphery. This delayed combustion approach also reduces peak flame temperatures which minimizes NO_x formed by thermal fixation of the nitrogen present in combustion air.

Tangentially-fired boilers require a different approach to achieve the same results. In this case, the coal and primary combustion air are introduced in a jet which penetrates most of the width of the furnace. The jet is directed along the tangent of an imaginary circle in the center of the furnace. Secondary air is introduced in the same vertical plane at

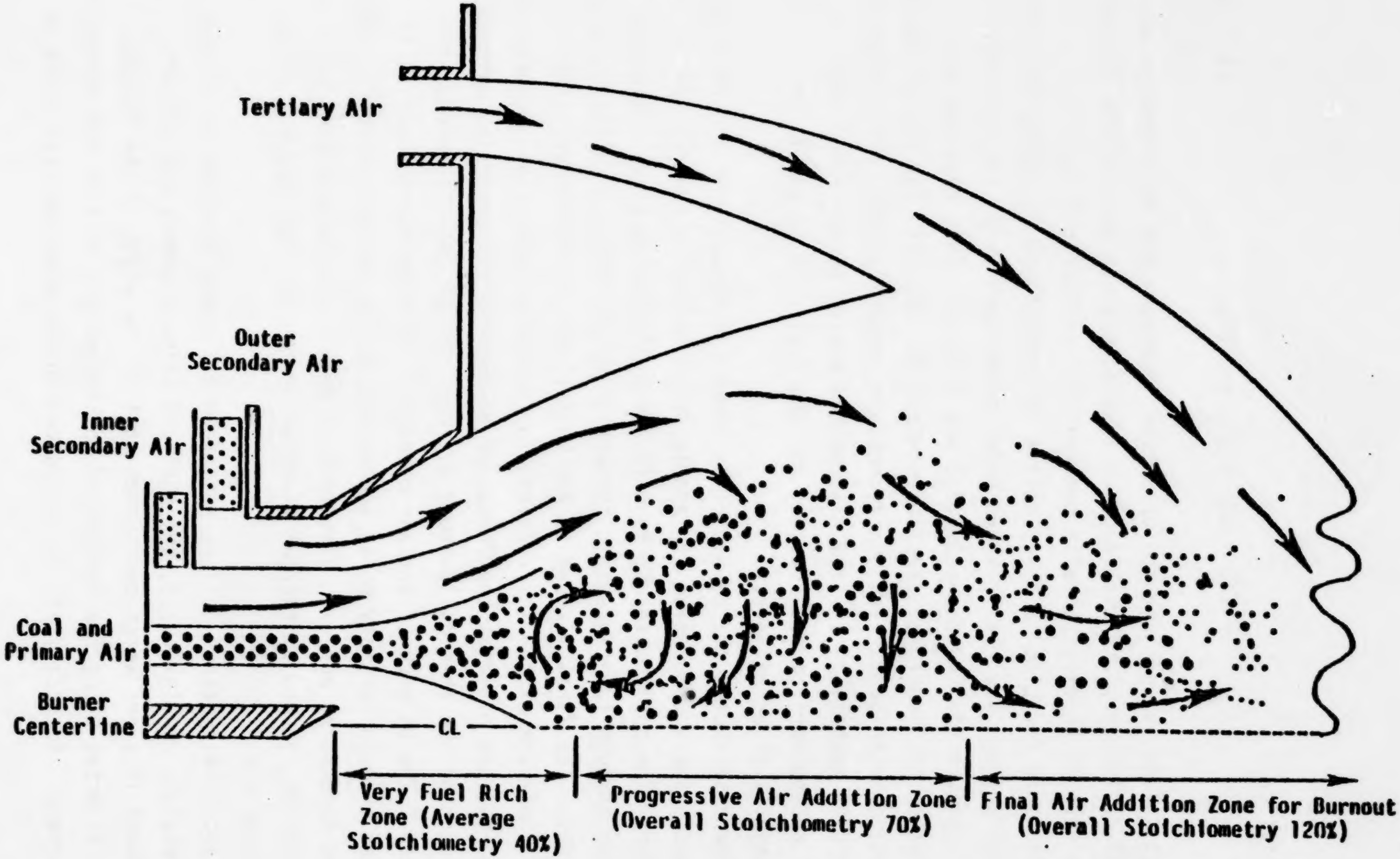

Tertiary Air
Outer Secondary Air
Inner Secondary Air
Coal and Primary Air
Burner Centerline
CL
Very Fuel Rich Zone (Average Stoichiometry 40%)
Progressive Air Addition Zone (Overall Stoichiometry 70%)
Final Air Addition Zone for Burnout (Overall Stoichiometry 120%)

Figure 3.2-1. Multistage combustion in a distributed mixing burner (top half of burner only depicted).[a]

[a] Figure redrawn from figure presented in reference 15.

elevations both above and below the fuel jet. The balance of the combustion air is introduced in the same horizontal plane as the fuel jets but directed at an angle closer to the furnace wall. By mounting one such assembly at each corner of the furnace, a fuel-rich fireball is formed in the center of the furnace. This design generates the same type of delayed mixing as the DMB and likewise reduced NO_x formation. In most boilers, multiple burner elevations are used to provide the necessary energy input. A plan view of the fuel rich fireball approach is shown in Figure 3.2-2.

3.2.2 Factors Affecting Performance

The variables which appear to have the greatest effect on the SO_2 capture rate are temperature, residence time and limestone stoichiometry (Ca/S ratio). Temperature effects are important because of their impacts upon both the thermodynamics and kinetics of the calcination and sulfur capture reactions. Temperatures substantially below about 800°C (1500°F) will cause the reactions shown in Equations 3.2.2-2 and 3.2.2-3 to proceed at rates which are too slow to be of commercial significance. Very high temperatures on the other hand (well above 1000°C) can deactivate the sorbent and lower the driving forces for sulfur capture. Because of these effects, the LIMB process achieves its best results when the sorbent is injected and the coal firing is controlled so that the residence time of the particles at the optimum temperatures for reaction is maximized. Some of the same conditions which favor efficient sulfur capture are also favorable from the standpoint of minimizings NO_x formation.

3.2.3 Applicability to Industrial Boilers

The current emphasis of LIMB technology is on utility application. The major factors influencing the compatibility of LIMB with new boilers appear to be the coal properties and the design of the boiler furnace, convection section, and ash removal system. Depending on these factors, potential problems arising from LIMB applications include increased

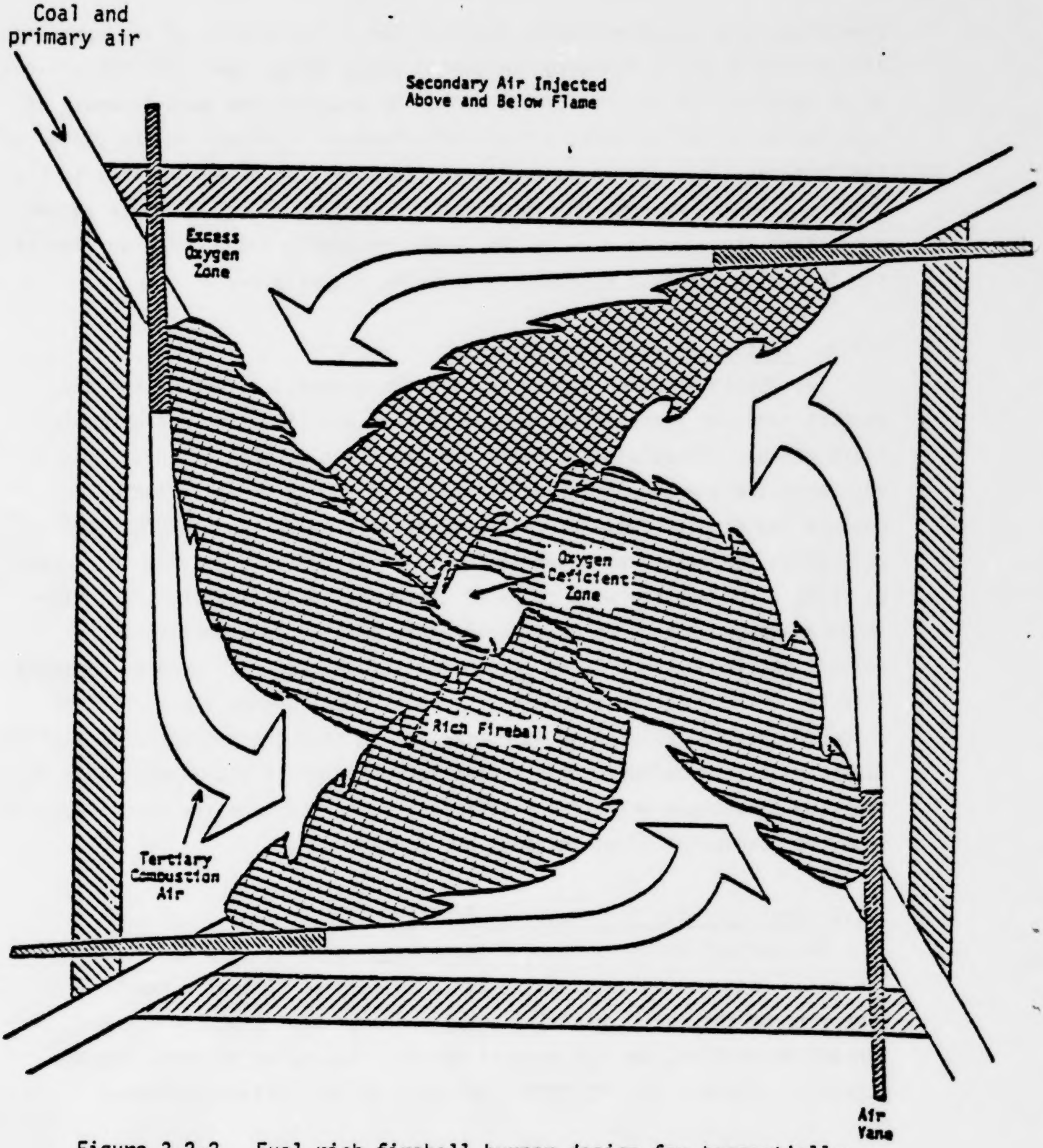


Figure 3.2-2. Fuel rich fireball burner design for tangentially fired boiler.

[a]Figure redrawn from figure presented in reference 15.

furnace slagging, plugging of tight convection section passes, overloading or plugging of ash removal systems, and incomplete coal combustion. These problems must be dealt with through alterations in boiler operating procedures or system design modifications. In addition, LIMB technology will also increase boiler thermal losses by 1 to 2 percent, and will require higher efficiency downstream particulate controls due to the increase in uncontrolled particulate matter emissions. It is expected that similar problems will have to be dealt with in applying LIMB to industrial boilers.

3.2.4 Development Status

A primary driving force behind LIMB technology development at present is the need for low cost, NO_x and SO_2 control systems for retrofit applications to pulverized coal boilers.

The largest scale test effort to date has been carried out by Dr. Klaus Hein of Rhienisch-Westfailsches Electrizitatswerk (RWE) in the Federal Republic of Germany. His work involved the firing of brown coal in tangentially-fired pulverized coal boilers. Brown coal is a low rank coal similar to a low quality lignite. These boilers operate at relatively low combustion zone temperatures due to the high moisture content of the coal (up to 60 percent) and the flue gas recirculation used for drying. These conditions are thought to be favorable for sulfur capture by the sorbent as well as the generation of relatively low NO_x emissions. This system was tested on a 60 MW_e boiler where SO_2 reductions of over 60 percent were achieved on a low sulfur coal. Tests on a 300 MW_e boiler are planned in 1982-83.

Other tests include those conducted by Steinmuller, a major German boiler manufacturer. Steinmuller ran bench-scale experiments using natural gas doped with sulfur compounds. They also conducted 2 MW_t pilot-scale tests with sulfur-doped natural gas and pulverized coal. The pilot-scale burner is a staged burner, the design of which is based on earlier EPA work on the distributed mixing burner. Using a proprietary calcium-based sorbent, Steinmuller has achieved up to 70 percent SO_x control at a calcium-to-sulfur stoichiometry of two-to-one.

The development of LIMB will continue to be affected by ongoing low NO_x combustion technique development efforts. First generation low-NO_x burners developed by various boiler manufacturers are already being installed on utility-scale coal-fired boilers. Further, EPA's low NO_x-program has produced very encouraging pilot-scale test results with more advanced burner designs such as the distributed mixing burner for wall-fired units and the fuel rich fireball for tangentially-fired units. Evaluations of a wall fired burner on an industrial boiler and of a tangential burner on a utility boiler are currently in progress. Results now show that NO_x emission levels from these advanced burners can be maintained at levels of 0.3 $lb/10^6$ Btu.

3.2.5 Emissions Data

Recent LIMB performance data were discussed in previous sections. No long term commercial scale performance data are available at present. LIMB testing on a 700 MW_e utility boiler in West Germany is planned for late 1983 and laboratory- and pilot scale testing by EPA is continuing.[15]

3.3 COAL/LIMESTONE PELLETS

Coal/limestone pellet technology is an SO_2 removal technique currently being developed by the EPA. In this process, coal/limestone pellets are fired as ordinary fuel in stoker boilers; the SO_2 formed during combustion reacts with the limestone present in the fuel pellets to form calcium sulfate and calcium sulfite salts.

No significant developments have occurred for this technology since the preparation of the March 1982 Industrial Boilers Background Information Document (BID).[6] A 14-day continuous test burn of the pellets had been scheduled for a 60,000 lb stream/hr chaingrate stoker boiler. However, the 14-day test has been cancelled or delayed indefinitely due to problems with the pellets as manufactured by Banner Industries.[16] Adequate drying of the pellets on a large-scale production basis was not possible with Banner's existing process equipment.

Work on the development of coal/limestone pellet technology has only recently been resumed and no new results are yet available.[17] Current research efforts are being directed toward the development of a coal/limestone briquette production process that will produce pellets with mechanical strength and durability characteristics superior to those produced using auger extrusion.[17]

3.4 REFERENCES

1. Makansi, J. and B. Schwieger. "Fludized-Bed Boilers." Power. 126(8):126. August 1982.

2. Hubble, B.R. Fluidized-Bed Combustion: A Review of Environmental Aspects. Argonne National Laboratory Report No. ANL/ECT-12. January 1982.

3. U.S. Environmental Protection Agency. Fossil Fuel Fired Industrial Boilers -- Background Information Document. EPA Report No. EPA-450/3-82-006. March 1982.

4. Golirsch, G.M., S.A. Benson, D.R. Hajicek, and J.L. Cooper. Sulfur Control and Bed Material Agglomeration Experience in Low-Rank Coal AFBC Testing. Volume II. Proceedings of the Seventh International Conference on Fluidized-Bed Combustion. Grand Forks Energy Technology Center/Combustion Power Company, Inc. October 1982. pp. 1107-1120.

5. Golirsch, G., et al. Atmospheric Fluidized Bed Combustion Testing of North Dakota Lignite. Volume III. Proceedings of the Sixth International Conference on Fluidized Bed Combustion. April 1980. pp. 850-862.

6. Schwieger, B. "Fluidized-Bed Boilers Keep Chinese Industry Running on Marginal Fuels." Power. 127(3):59-61. March 1983.

7. Mares, J.W. Keynote Address. Proceedings of the Seventh International Conference on Fluidized-Bed Combustion. Volume I. U.S. Department of Energy. October 1982. pp. 1-4.

8. Aul, E.F. Notes from meeting between Radian Corporation and U.S. Department of Energy/Morgantown Energy Technology Center, Morgantown, West Virginia. June 14, 1983.

9. Young, C.W., et al. Continuous Emission Monitoring at the Georgetown University Fluidized Bed Boiler. Publication No. EPA-600/S7-81-078. March 1983.

10. Castleman, J.M., et al. Campaign I Report: Technical Summary of TVA/EPRI 20-MW AFBC Pilot Plant Test Program. Volume I. TVA/Energy Demonstrations and Technology Division. May 1983.

11. Fraser, R.G. Operation and Testing of the Wormser Grate Fluidized Bed Combustor at the USM Corporation at Beverly, Massachusetts. Publication No. DOE/ET/15460-193. May 1981.

12. Sadowski, R.S., et al. (Wormser Engineering, Inc.) Operating Experience with a Coal-Fired Two Stage FBC in an Industrial Plant. (Presented at the 76th Annual Meeting of the Air Pollution Control Association. June 1983.)

13. Lund, T. (Lurgi Corporation.) Lurgi Circulating Fluid Bed Boiler: Its Design and Operation. Volume I. Proceedings of the Seventh International Conference on Fluidized Bed Combustion. October, 1982. pp. 38-46.

14. Jones, O. and E.C. Seber. (Conoco, Inc.) Initial Operating Experience at Conoco's South Texas Multi-Solids FBC Steam Generator. Volume I. Proceedings of the Seventh International Conference on Fluidized Bed Combustion. October 1982. pp. 381-389.

15. Brna, T. G. and G. B. Martin. New Development: Dry Flue Gas Desulfurization and Combined SO_x and NO_x Removal. (Presented at the Third E.C.E. Conference on Desulfurization of Fuels and Combustion Gases. Salzburg, Austria. May 18-22, 1981.) 36 pp.

16. Kelly, M. E. and S. A. Shareef (Radian Corporation). Third Survey of Dry SO_2 Control Systems. (Prepared for U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina, Publication No. EPA600/7-81-097. June 1981.

17. Letter from J. A. Maddox (Radian), to Jack Wasser (IERL), May 23, 1984. Status of Coal/Limestone Pellet Technology.

4.0 PRECOMBUSTION CONTROL APPROACHES

Precombustion control techniques for reducing PM, NO_x, and SO_2 emissions from industrial boilers include physical or chemical coal cleaning and the production of clean synthetic gaseous or liquid fuels from coal. Recent developments impacting the applicability of these technologies to industrial boilers are summarized in this section.

The use of coal-liquid mixture (CLM) as industrial boiler fuels is also discussed in this section. While CLM use is not a control technique per se, this treatment reflects the recent interest shown in CLM's for liquid fuel-fired boiler retrofit applications.

4.1 PHYSICAL COAL CLEANING

Physical coal cleaning (PCC) or coal washing is a cost competitive method of reducing the sulfur and ash contents of coals containing significant quantities of pyrite sulfur and/or ash. Several recent economic studies have indicated that it may be possible to reduce coal sulfur levels with PCC at no net cost to the fuel purchaser. This finding result from the credits which can be taken for reduced coal transportation costs, reduced ash and scrubber sludge disposal costs, reduced FGD system reagent requirements, reduced boiler maintenance costs, and increased boiler efficiency and operability which result from the use of a higher grade coal. These costs can more than offset the costs of the coal cleaning plant.[1]

4.1.1 Process Description

In a modern PCC plant, coal is typically subjected to size reduction and screening, separation of coal-rich and impurity-rich fractions, dewatering, and drying. Commercial PCC methods achieve a separation of the coal from its impurities by relying on differences in the specific gravity (gravity separation) or the surface properties of the coal and its mineral matter (froth flotation).

The overall process design philosophy in most modern PCC plants is to treat precise fractions of the crushed coal feed with specific unit operations which best meet the overall cleaning plant objectives. A characteristic of this design philosophy is that multiple product streams evolve, each with its own set of physical and chemical properties. These separate product streams may be blended prior to shipment to produce a composite coal precisely meeting the consumer's specifications. Within the context of supplying small industrial boilers, many opportunities exists for premium (low-ash, low-sulfur) size fractions to be segregated from the final blending operation and targeted for specific end users.[2]

4.1.2 Factors Affecting Performance

The primary factor which determines the amount of sulfur reduction which is achievable by physical cleaning is the distribution of the sulfur forms in the coal. There are three general forms of sulfur in coal; pyritic, sulfate, and organic. Pyritic sulfur generally exists as individual particles (0.1 micron to 25 cm in diameter) distributed uniformly through the coal matrix. Pyrite is a dense mineral (4.5 g/cc) compared with bituminous coal (1.3 g/cc) and is not water-soluble; the best means of removing pyrite sulfur from coal is by specific gravity separation (dense media washing).

Sulfate sulfur is usually present in very small amounts (0.1 percent by weight or less) in coal. This form of sulfur, is usually water soluble and can be removed by washing the coal.

Organic sulfur is usually chemical bonded to the organic carbon of the coal and cannot be removed unless the chemical bonds are broken. The amount of organic sulfur present thus defines the lowest limit to which a coal can be cleaned with respect to sulfur removal by physical methods.[3]

Other factors affecting the performance of PCC technology include: the size to which the coal is crushed, the unit processor employed, the densities of the separating media and the percent recovery of cleaned coal on a mass or energy input basis. Higher removal percentages can be achieved only at the cost of lower mass or energy recovery rates (higher percent rejected material).

4.1.3 Applicability to Industrial Boilers

The firing of physically cleaned coal in industrial pulverized coal-fired boilers offers several advantages over the use of raw coal. Because physical cleaning partially removes pyrite, ash, and other impurities, both SO_2 and particulate emissions are reduced. Physical cleaning also results in the production of fuel with much more uniform properties than the raw coal (see Figure 4.1-1). This results in greatly improved combustor performance characteristics. As compared to raw coal, physically cleaned coal is easier to handle and feed, and burns more efficiently and uniformly with less chance for clinkering. This reduces boiler maintenance and ash disposal problems. Physical cleaning of coal should also improve the overall performance of stoker-fired boilers provided the resultant coal size is acceptable for stoker firing.

4.1.4 Development Status

As shown in Table 4.1-1, over 224 million tons of bituminous coal and lignite were cleaned by mechanical means in 1978, the last year for which cleaning plant statistics were developed. This represents about one third of the total US. production of bituminous coal and lignite for that year. The majority of the cleaning plants currently in operation are designed for ash removal rather than sulfur removal, although many take out 20-30 percent of the sulfur in the raw coal. The capabilities of individual plants vary widely from less than 200 to more than 25,000 metric tons per day.[6]

Most of the PCC plants which are currently in service operate with fairly low capacity factors. This characteristic is due to a combination of two effects:

- the fluctuating (e.g. seasonal) nature of coal demands and
- the maintenance requirements associated with any solids handling operation.

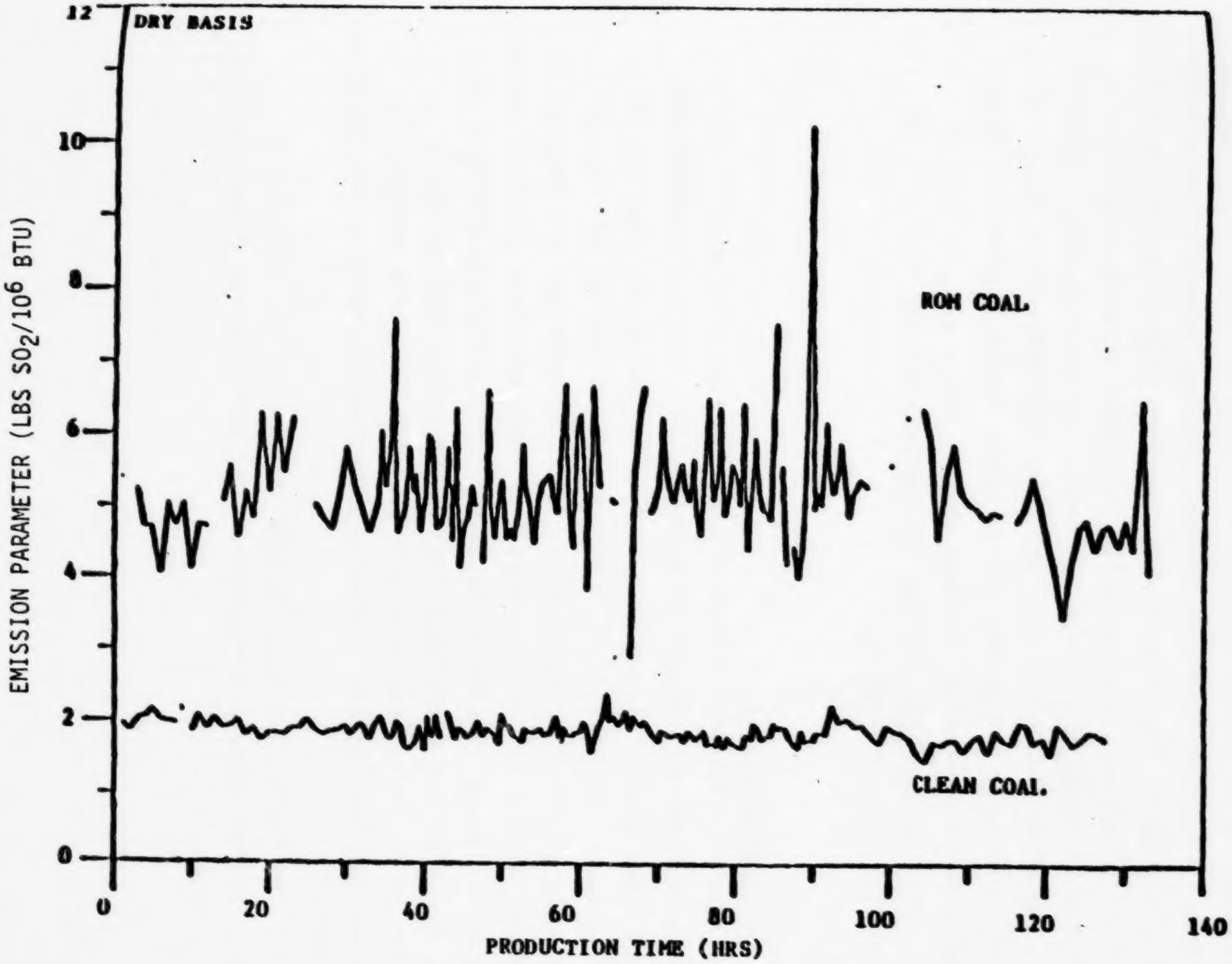


FIGURE 4.1-1 Kitt Mine Coal Preparation Plant - Hourly Incremental Data for Sulfur Dioxide Emission Parameter

(Source: Reference 4).

TABLE 4.1-1. PREPARATION AND THERMAL DRYING OF BITUMINOUS COAL AND LIGNITE BY STATE - 1978 (Thousand Short Tons)

	Number of Cleaning Plants	Mechanically Cleaned	Crushed or Screened	No Processing	Total a/ Production	Number of Thermal Drying Units	Tons Thermally Dried
Alabama	28	8,584	2,974	8,996	20,553	1	414
Alaska	1	59	525	147	731	-	-
Arizona	-	-	9,054	-	9,054	-	-
Arkansas	2	109	202	208	519	-	-
Colorado	4	2,584	8,764	2,466	13,814	1	881
Georgia	1	-	89	24	113	-	-
Illinois	37	38,691	9,554	355	48,600	6	3,852
Indiana	14	15,767	4,868	3,547	24,182	-	-
Iowa	1	-	361	89	450	-	-
Kansas	2	652	512	62	1,226	-	-
Kentucky:							
Eastern	50	26,380	55,043	14,810	96,233	7	2,094
Western	14	14,170	20,650	4,636	39,456	1	373
Total	64	40,550	75,693	19,446	135,689	8	2,467
Maryland	1	38	1,164	1,797	2,998	1	37
Missouri	3	1,023	2,493	2,150	5,665	-	-
Montana	-	-	17,535	9,065	26,600	-	-
New Mexico	1	665	11,381	586	12,632	-	-
North Dakota	-	-	9,245	4,783	14,028	1	75
Ohio	18	16,550	13,378	11,309	41,237	6	603
Oklahoma	5	457	4,765	847	6,070	2	175
Pennsylvania	66	35,546	31,578	14,353	81,477	15	2,926
Tennessee	2	1,568	5,743	2,721	10,032	1	100
Texas	1	1,417	18,332	271	20,020	9	1,417
Utah	6	2,641	5,869	630	9,141	1	150
Virginia	24	8,953	14,986	8,007	31,946	17	2,293
Washington	2	4,708	-	-	4,708	-	-
West Virginia	135	44,186	27,884	13,244	85,314	49	7,892
Wyoming	1	34	55,405	2,889	58,328	-	-
Total United States a/	419	224,780	332,353	107,994	665,127	118	23,282

a/ Data may not add to totals shown due to independent rounding.

(Source: Reference 5).

4.1.5 Performance

PCC will typically remove about 50 percent of the pyritic sulfur present in coal, although the actual removal will depend on the washability of the coal (the ratio of pyritic to organic sulfur), the size to which the coal is crushed, the unit processes employed, and the densities of the separating media.[7] An analysis of levels and forms of sulfur found in typical U.S. coals indicates that the high sulfur bituminous coals mined in the northern appalachian and midwestern states typically contain up to 70 percent pyritic sulfur. As much as 70 percent of this sulfur can be removed in cleaning processes which achieve a 90 percent recovery of the energy content of the input coal. Coals from the southern appalachian and western coal producing states more typically contain about 30 to 40 percent pyrite sulfur. When these coals are cleaned by physical methods, total sulfur reductions of about 20 to 30 percent (calculated on a $lb/10^6$ Btu basis) are typically achieved.

4.2 COAL GASIFICATION

A number of commercially available coal gasification/gas purification technologies have been proven to be capable of substantially reducing the emissions of SO_2, PM and NO_x that result from the direct combustion of coal. At the present time, however, there is limited interest in the construction of new gasification facilities to produce fuel gases for new industrial boilers. The primary reason for this lack of interest is the current low cost (relative to coal-derived gases) and high availability of natural gas from conventional sources.

The key to the SO_2 control capability of a coal gasification system is the performance of the acid gas removal (AGR) unit of the gas purification section of the plant. Industrial boiler fuel supply systems requiring an AGR unit will generally not be cost competitive with conventional natural gas, oil, or coal-fired boilers equipped with post-combustion controls. This will limit most new gasifier applications to systems requiring a non-interruptable gaseous fuel supply which do not have stringent product gas sulfur specifications.

4.2.1. Process Description

As shown in Figure 4.2-1, a complete gasification-based fuel production system (including pollution control) consists of three steps: coal pretreatment, coal gasification and gas purification. Coal pretreatment is necessary to supply a feedstock with the proper physical and chemical characteristics to the gasifier. In the gasification step, pretreated coal is reacted with a steam/air or steam/oxygen mixture to produce a gas with a heating value of approximately 5.6 MJ/Nm^3 (150 Btu/scf) in the air-blown (low Btu) case or 13 MJ/Nm^3 (350 Btu/scf) in the oxygen-blown (medium-Btu) case. In the gas purification step, particulate matter (including condensed heavy hydrocarbons), sulfur and nitrogen species may be removed from the raw product gas. The extent of gas purification required is determined by the desired end use of the product gas and/or the applicable emission standards for the end use combustion equipment.

4.2.2 Factors Affecting Performance

The most critical parts of a coal gasification system from the standpoint of final fuel gas specifications (which in turn determine the ultimate emissions from any downstream process) are the gas scrubbing and acid gas removal (AGR) operations. Removal of coal dust, ash, and tar aerosols entrained in the raw product gas leaving the gasifier can be accomplished with cyclones, or ESPs, or with water, oil or solvent scrubbers. In the gas quenching and cooling section, tars and oils can be condensed and particulates and other impurities, such as ammonia, sulfides and cyanides can be scrubbed from the raw product gas.

Acid gases such as H_2S, HCN, COS, CS_2, mercaptans, and SO_2 are only partially removed from a raw fuel gas in a simple gas quenching and cooling section. For this reason, either low sulfur coal or an AGR system must be used to significantly reduce the level of sulfur emissions in a boiler flue gas stream. Commercially available AGR techniques include physical and chemical solvent (absorption) processes, direct conversion, catalytic conversion processes and fixed-bed adsorption processes. The specific gas

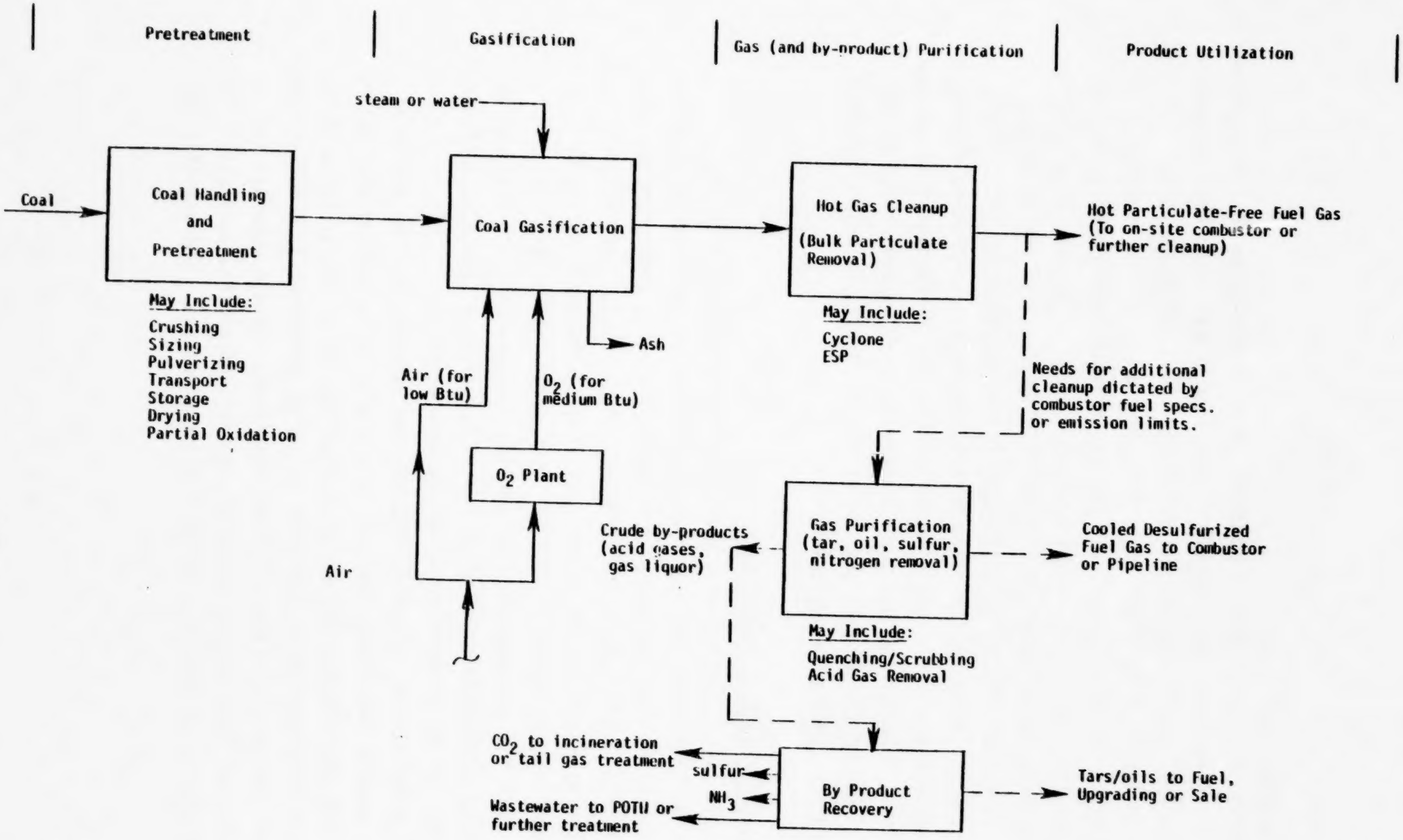

Pretreatment
Gasification
Gas (and by-product) Purification
Product Utilization
Coal
Coal Handling and Pretreatment
May Include:
Crushing
Sizing
Pulverizing
Transport
Storage
Drying
Partial Oxidation
steam or water
Coal Gasification
Ash
Air (for low Btu)
O2 (for medium Btu)
O2 Plant
Air
Hot Gas Cleanup
(Bulk Particulate Removal)
May Include:
Cyclone
ESP
Hot Particulate-Free Fuel Gas (To on-site combustor or further cleanup)
Needs for additional cleanup dictated by combustor fuel specs. or emission limits.
Gas Purification (tar, oil, sulfur, nitrogen removal)
May Include:
Quenching/Scrubbing
Acid Gas Removal
Crude by-products (acid gases, gas liquor)
Cooled Desulfurized Fuel Gas to Combustor or Pipeline
By Product Recovery
CO2 to incineration or tail gas treatment
sulfur
NH3
Wastewater to POTW or further treatment
Tars/oils to Fuel, Upgrading or Sale

Figure 4.2-1. Low/medium-Btu gasification process options for supplying an industrial boiler fuel gas.

cleanup process used will generally depend on the raw fuel gas pressure and composition as well as the desired levels of contaminant removal.

Essentially complete removal of the particulate matter and reduced nitrogen species present in the quenched raw product gas stream will be achieved in most commercial AGR system. The level of reduced sulfur species removal which is achieved will be dictated by the SO_2 emission limits of the combustor. In synthesis gas applications, product gas specifications for residual sulfur species concentrations are typically 1 ppm or less and these levels have been achieved in commercial systems. Since combustion applications do not usually require these stringent removal levels, so commercial AGR units for fuel gas production units can be designed for almost any desired level of removal of the reduced sulfur present in the quenched raw gas.

4.2.3 Applicability to Industrial Boilers

Low- and medium-Btu gasification systems are applicable to any industrial boiler that can accept a gaseous fuel. Since low-Btu gas combustion requires higher fuel flows and generates higher flue gas volumes than natural gas on an equivalent energy input basis, new boilers will have to be equipped with slightly larger fuel and flue gas handling systems to burn low-Btu gas. Otherwise, there are no technical obstacles to the use of low- or medium-Btu gas as a boiler fuel.

In most cases, the use of low- or medium-Btu gas as an industrial boiler fuel will be more costly than a direct-coal-fired unit equipped with post combustion controls. Because of these economic considerations, most future gasification system applications will not involve a dedicated fuel gas production facility for a new industrial boiler. Future applications, like current ones, are more likely to involve direct process heating where (1) a clean gaseous fuel is required and (2) a non-interruptable supply of natural gas is not available or cannot be guaranteed.

4.2.4 Development status

There are only a limited number of coal gasifiers operating in the United States on a commercial basis at the present time (see Table 4.2-1). Most of these units are used to produce fuel gas for process heaters or furnaces. Two of the units were designed to produce fuel gas for an industrial boiler. These are the UMD/Foster Wheeler/Stoic and the Can-Do facilities. It should be noted that both of these units were constructed with significant support funds provided by the U.S. DOE.

Only two of the gasification systems listed in Table 4.2-1 are equipped with gas cleanup systems that include acid gas removal units. Both of these systems utilize Stretford AGR/sulfur recovery technology. The Allis Chalmers demonstration unit, which is designed to supply approximately 400 x 10^6 Btu/hr of low Btu fuel gas to a utility boiler, is now undergoing startup. The Caterpillar Tractor AGR unit operated at reduced loads (less than 40 percent of design) during the 1979-1982 time frame but this unit has since been shut down indefinitely.[1]

4.2.5 Reliability

Because of the limited commercial operating history of coal gasification/gas purification systems in this country, there are no detailed statistics on the frequency and severity of operating problems with these units. The Caterpillar Tractor Stretford system apparently experienced no significant operating problems during its two-plus years of operation, but this system never operated above 40 percent of its design load.[8] The numerous gasifiers which are currently operating around the country have a long history of reliable operation. However, this experience is not necessarily applicable to units equipped with extensive gas cleanup facilities.

4.2.6 Emissions Data

No certified test data for the Caterpillar Tractor AGR system are available. This unit was not operated under any regulatory constraints and there were no requirements for routinely reporting any fuel gas quality or

TABLE 4.2-1. CURRENT APPLICATIONS OF LOW AND MEDIUM BTU GASIFICATION TECHNOLOGY

Facility	Gasifier and Coal Type	Extent of Product Gas Clean-up and Fuel End Use
Commercial Units-Domestic		
Holston Army Ammunition Plant Kingsport, TN	Ten, air-blown Chapman gasifiers; bituminous coal	Hot cyclone; quenching; scrubbing; gas used as fuel in process furnace; tar burner in boiler.
Glen-Gery Brick Company; Nine sites in Eastern, PA	Twelve, air-blown Wellman Galusha gasifiers, anthracite	Hot cyclone; hot gas used as brick kiln fuel
National Lime and Stone, Co. Cary, OH	Two, air-blown Wellman Galusha gasifiers; bituminous coal	Hot cyclone; hot gas used as lime kiln fuel
Caterpillar Tractor York, PA	Two, air-blown, Wellman incandescant gasifiers; bituminous coal	Quenching; scrubbing; ESP; AGR (Stretford); gas used as process heater fuel.
University of Minnesota Duluth, MN	One, air-blown, Foster-Wheeler/ Stoic gasifier	Hot cyclone; ESP; quenching; scrubbing; gas used as boiler fuel; tars incinerated
Allis Chalmers East Alton, IL	One, air-blown, Kilngas gasifier	Hot cyclone; quenching; scrubbing; AGR (Stretford); gas used as utility boiler fuel
Can Do, Inc. Hazelton, PA	Two, air-blown Wellman Galusha gasifiers; anthracite	Hot cyclone; cooling; gas used as fuel for industrial park
Howmet Aluminum Lancaster, PA	One, air-blown Wellman Galusha gasifier; anthracite	Hot cyclone; gas used as process heater fuel
Elgin-Butler Brick Co. Austin, TX	One air-blown SSF gasifier; lignite	Hot cyclone; gas used as brick kiln fuel

TABLE 4.2-1. CURRENT APPLICATIONS OF LOW AND MEDIUM BTU GASIFICATION TECHNOLOGY
(Continued)

Facility	Gasifier and Coal Type	Extent of Product Gas Clean-up and Fuel End Use
Commercial Units - Foreign		
Numerous foreign facilities in Europe, Asia and Africa	Lurgi and Koppers-Totzek are the most widely used commercial systems; low rank coals generally used as feedstocks.	As needed to meet process requirements; synthesis gas and industrial fuel gas are the most common applications.
Developmental Units - Domestic and Foreign		
Numerous systems are under development both in the U.S. and abroad which offer the potential for improvements in operating efficiency, reliability, fuel flexibility, environmental control effectiveness or cost effectiveness relative to competitive technologies. These technologies have not reached a stage of development which would be characterized as commercially demonstrated however: BGC/Lurgi and GFETC slagging gasifiers, Westinghouse, U-gas, Pressurized Wellman Galusha (METC), Exxon (Catalytic), Bigas, GEGAS, Shell (Koppers) and Texaco.		

combustor flue gas emissions data. The operators of this system claim, however, that they had no problems in meeting the design outlet fuel gas sulfur specification of less than 10 ppm total reduced sulfur.

4.3 COAL-LIQUID MIXTURES

A coal-liquid mixture (CLM) is any blend of coal, liquid fuels (e.g. fuel oil, methanol), water and additives (dispersants) that allows coal to be handled as a liquid rather than as a solid fuel. The objective in using CLMs is to substitute a less expensive, readily available solid fuel for a more expensive, premium liquid fuel. With coal-water slurries (CWS), total substitution of coal for oil is achieved whereas only partial substitution is achieved with coal-oil (COM) or coal-oil-water (COW) mixtures. Because of the economic advantages of a complete substitution for oil, recent interest in the use of CWS has been increasing at the expense of COM and COW use.

The main applications of CLMs are expected to be in retrofits of existing oil-fired boilers. In new applications, a conventional coal-fired unit will generally be more cost effective. Incentives for converting existing oil-fired boilers to CLM firing are provided by the lower cost of coal on an equivalent energy input basis and concerns over the future availability and price of premium liquid fuels. Another consideration is the compatibility of CLM technology with deep coal cleaning methods (as discussed in Section 4.1). Since both of these technologies require finely ground coal, coal cleaning techniques which will improve the quality of the final CLM blend can be easily and cost effectively integrated into a CLM preparation plant.

In most applications, there will be no direct environmental benefits associated with the use of CLMs. Uncontrolled PM and SO_2 emissions from CLM-fired boilers are similar in character and present in quantities that are predictable from the properties of the parent fuels. Uncontrolled emissions of NO_x with CWS-firing will be reduced due to the effect of water in lowering the flame temperature. This benefit is not realized, however, when staged combustion techniques are used for NO_x control. Any environmental benefits derived from CLM-firing are associated more with the use of a cleaned coal or an SO_2 adsorbent as a fuel additive than the use of a CLM directly.

4.3.1 Process Description

Preparation of coal-oil mixtures (COM), coal-water slurries (CWS), or coal-oil-water (COW) mixtures involves several steps. Coal pulverizing and blending of the mixtures may be done either on-site or off-site depending on the sizes of the units involved and a number of other site-specific factors. In most small boilers, the CLM fuel would be prepared off-site in a large centralized preparation plant and transported to the end-user in order to realize the most favorable cost savings. A typical, large COM plant producing 10,000 bpd of a 50/50 (wt./wt.) COM mixture would supply the fuel input needs of approximately 750 MW_t (2500 x 10^6 Btu/hr) of industrial boiler capacity.

All coal-liquid mixtures are prepared by grinding the feed coal to a very fine mesh size (usually to at least 70 percent through 200 mesh) prior to preparing the final CLM blend. A finer grind provides better fuel stability (less tendency for the coal particles to settle), better combustion characteristics and reduced erosion problems in the fuel handling/ feeding system. One utility boiler application in Florida, for example, has tested a coal-oil mixture (COM) with a coal feed ground to 98 percent through 325 mesh.[9] The disadvantages of a smaller grind size include: higher grinding costs, a higher fuel viscosity (which will impact the design of the fuel pumping, agitation and atomization systems) and potentially the generation of finer fly ash particulates in the combustion flue gas.

The choice of a final blend mixture is dictated by a complex set of site-specific constraints and economic trade offs. Generally the maximum fuel savings is realized by maximizing the coal and minimizing the liquid fuel content of the final blend mixture. With CWSs in particular, a high coal content is required in order to maintain an acceptable furnace efficiency. CWSs containing up to about 75 percent (wt.) coal have been tested to date.[10] COM blends are not limited by these same thermal efficiency constraints and so mixtures containing as little as 10 percent (wt.) coal have been tested.[11] The maximum practical coal content of a COM is limited by coal handling pumping, erosion and viscosity concerns to about 50 percent (wt.) coal.

4.3.2 Factors Affecting Performance

The most important factors which affect the performance of a CLM-fired boiler from an emissions point of view are the characteristics of the fuels fired in the boiler and the capabilities of the control devices applied to the unit. Generally, about 80 percent of the ash and 90-plus percent of the sulfur present in a fuel will leave a boiler as flue gas particulate and SO_2 emissions respectively. Since most CLMs will have a higher ash content and may have a higher sulfur content than the fuel oils they replace, additional control equipment for both PM and SO_2 may be needed. Careful fuel selection and blending or the use of fuel cleaning technologies upstream of the CLM blending step could minimize or eliminate the need for additional SO_2 control equipment. However, most boilers converted from oil to CLM's will need additional PM controls.

CLMs contain about 1 percent additives and stabilizers, which are often alkaline compounds. Although these additives may reduce SO_2 slightly by reacting with SO_2 to form sulfate and sulfate salts, their use increases flue gas PM loadings and may contribute to increased furnace slagging, fouling and refractory degradation problems. For these reasons, CLM producers are examining the use of alternative additives such as ammonium-based compounds.

4.3.3 Applicability to industrial boilers

Almost any liquid fuel-fired boiler can be converted to burn CLMs. The types of modifications that may be needed to accomplish this conversion include: the addition of an agitator and possibly a heater to the liquid fuel storage tank, additional liquid fuel pumping capacity (larger pumps and possibly larger fuel supply lines), modified burners with special erosion resistant tips, additional steam for soot blowing and fuel atomization, modifications to the furnace bottom and ash handling system to accommodate higher ash flows, and new or upgraded flue gas treatment equipment to maintain compliance with applicable environmental regulations. Also, some derating of the boiler may be necessary in order to provide enough residence time for the slower coal combustion reactions to occur. Because of these considerations, the units which are best suited for a conversion to CLM-firing are those which were originally designed for coal firing (with "V" step bottoms, low plan area heat release rates, low furnace liberation rates and adequate equipment for handling increased flue gas and ash loadings). Typical conversion costs for units which are reasonable candidates for CLM-firing were estimated to be in the range of \$100-150/kW in one recently published study, while costs for equivalent new coal-fired units were determined to be about \$500/kW.[12]

4.3.4 Development Status

Most of the CLM development, testing and demonstration work which was done in the late 1970's was focused on coal-oil mixtures rather than coal-water slurries. By 1981, COMs containing up to 50 percent (wt.) coal had been tested in a 400 MW_e utility boiler during a 1-year demonstration program.[13] According to another report, 21 units representing nearly 5000 MW_e of electric utility generating capacity have been converted to CLM-capable units and another 10,000 MW_e of conversions are planned.[14] No equivalent statistics on industrial boiler conversions were found although COMs have been tested in several industrial package boilers ranging in size up to about 35 MW_t (120 x 10^6 Btu/hr). Table 4.3-1 summarizes the recent test experience with COMs in package watertube boilers. Current locations and sizes of domestic COM preparation plants are shown in Table 4.3-2. Based upon the above facts, COM preparation, handling, and combustion technology is considered to be commercially proven.

Coal-water slurries did not receive nearly as much attention as COMs during the last 1970's. This was due primarily to concerns about the feasibility, costs and impacts (e.g., derating) of converting existing oil-fired boilers with limited ash handling and pollution control capabilities to coal-only firing. However, recent design studies indicate that unit deratings of only 3.5-5.5 percent are obtained when coal-water slurries containing 65-75 percent (wt.) coal are fired in a furnace with an adequate

TABLE 4.3-1. TEST EXPERIENCE WITH COM-FUELED PACKAGE WATERTUBE BOILERS

COMPANY	BOILER		FUEL	MODIFICATION	OPERATING EXPERIENCE	STATUS
	MFG	TYPE				
GM Saginaw, MI.	C. E. Wickes 120,000 lb/hr (preheater)	A	COM 35/50% coal	• Forney Verloop burner • Fuel storage and handling	Phase I - 250 hrs., 35% coal; Phase II. 494 hrs., 50% coal; 75% maximum load	Completed 1977
PETC Pittsburgh, PA	Nebraska 24,000 lb/hr	D	COM 40% coal	• Coen burner • Fuel storage and handling • Soot blower in convection pass • Baghouse • ID fan	500 hrs. over approximately two months; considerable ash accumulation in furnace	COM tests completed 1981; currently conducting CW tests
Island Creek Coal/Hooker Chemical White Springs, FL	B&W 120,000 lb/hr	D	COM 50% coal (COM Energy)	• Modified burners • Modified fuel handling system • Additional soot blower • Economizer • Baghouse • ID fan	Short term tests performed; evaluated effect of particle size on burner erosion	Long term tests planned
Humko Products Champagne, IL	C. E. Wickes 40,000 lb/hr	A	COM 35% coal (ERGON) 50% coal (Coaliquids)	• Howe Baker burner • Fuel handling system	Short term tests up to full load satisfactory	Completed in 1978.
ERGON Vicksburg, MS	Superior 125,000 lb/hr	D	COM 35% coal	• Modified nozzle in Howe Baker burner • Fuel storage and handling	Used to provide process steam for fluid energy mill	Initial operation completed in 1981; fuel development continuing

Source: Reference [15]

TABLE 4.3-2. INSTALLED AND ANNOUNCED DOMESTIC COM PLANTS[a]

UNIT	LOCATION	STABILIZATION	BPD	CONSTR.	OPER.
INSTALLED					
Nepsco	Salem Harbor, MA	Chem.	2,000	1978	1979
Coal Liquid	Shelbyville, KY	Cottell	1,500	1978	1979
Florida Power & Light	Sanford, FL	Chem.	10,000	1979	1980
Ergon	Vicksburg, MS	Ultrafine	5,000	1980	1980
ANNOUNCED					
Ashland Oil	Southpoint, Oh	Chem.	1,200	1980	1981
COMCO	Bartow, FL	Ultrafine	3,000	1980	1981
Island Creek Coal	Jacksonville, FL	Chem.	3,000	1981	1981
Coal Liquid	Jacksonville, FL	Cottell	6,000	1981	1982
Mt. Airy	Dravosburg, PA	Cottell/Chem	1,500	1981	1982
Belcher	Mobile, AL	Chem./Mech.	5,000	1981	1982
Wyatt	New Haven, CT	Chem./Fine	3,000	1981	1982
Amcom	Chester, PA	N/A	3,000	1981	1982
Arco	West Virginia	Chem.	5,000	1981	1982

CUMULATIVE COM CAPACITY - BPD

ACTUAL		
1979	-	3,500
1980	-	18,500
FORECAST		
1981	-	25,700
1982	-	49,200

---

[a] Source: Reference 16

combustion volume.[17] Because of the feed coal size reduction requirements of CWS, deep coal cleaning technology can be easily integrated into a CWS preparation plant. This potential to generate a low ash, reduced sulfur, liquid fuel through the combined use of coal cleaning and CWS technology is one driving force behind much of the current CWS research, development and commercialization activities.

CWS technology would best be characterized as near commercial at the present time. The current U.S. CWS preparation plant capacity of only 40,000 tons/year will limit the number and scale of near-term CWS demonstration projects.[18] However, several recent tests have demonstrated the feasibility of CWS firing in commercial-scale equipment. A 75 percent (wt.) CWS has been successfully test-fired in a 12 MW_t (40×10^6 Btu/hr) industrial boiler.[19] Another report indicates that a 70 percent (wt.) CWS has been successfully fired in a 23 MW_t (80×10^6 Btu/hr) test burner.[20] EPRI and DOE are jointly sponsoring a CWS combustion test in a 65 MW_t (225×10^6 Btu/hr) industrial boiler in September, 1983.[21]

To date, there has been almost no commercial interest in coal-alcohol mixtures due to the high costs of fuel grade alcohols relative to those of petroleum-based fuel oils. Coal alcohol mixtures containing up to 40 percent (wt.) methanol have been burned successfully in a 1.5 MW_t (5×10^6 Btu/hr) industrial boiler.[22]

4.3.5 Reliability

No data defining the operating histories of commercial-scale systems firing CWS, COM, or COW mixtures have been published.

4.3.6 Emissions Data

Measurements of the emissions from a 65 MW_t (225×10^6 Btu/hr) CWS-fired industrial boiler in Memphis, Tennessee were conducted in September 1983. Results from these tests will be available in early 1984.

4.4 COAL LIQUEFACTION

Technical developments among coal liquefaction processes in the past five years have occurred primarily at the pilot plant scale as no large demonstration scale or commercial scale facilities have been constructed. The major technical advances that have occurred are the addition of two-stage liquefaction (TSL) to the SRC-I process and the use of solvent deashing for the SRC-I and H-Coal processes.

No firm commitments have been made at this time for the construction of a commercial-size coal liquefaction plant that could supply fuels to the industrial boiler market, although a number of proposed plants are in the advanced planning stages. Given the long construction and start-up lead times for plants of this type, no significant volumes of coal-derived liquid fuels will be available to industrial boiler owners in the next five years and probably not in the next ten years.

Emissions data from test burns with coal-derived liquids indicate that (1) SO_2 emissions depend on the sulfur content and heating value of the coal liquid (which can be adjusted by varying the liquefaction process operating conditions); (2) NO_x emissions are higher than comparable petroleum-derived fuels owing to the higher nitrogen content of coal liquids; and (3) uncontrolled PM emissions are comparable to petroleum-derived fuels but will probably require control by fabric filter rather than ESP due to low ash resistivity.

4.4.1 Process Description

As described in the Synthetic Fuels ITAR, coal liquefaction processes can be divided into two general categories: direct and indirect.[23] The indirect processes, also known as catalytic synthesis, gasify coal to generate a synthesis gas which is subsequently converted over a catalyst to a wide variety of fuels. Since the catalytic synthesis process starts with carbon monoxide and hydrogen, lower molecular weight products are favored such as LPG, gasoline, and diesel oil. Economic considerations dictate against the production of fuel oils that would be of interest to industrial boiler owners. Moreover, no commercial indirect liquefaction plants are operating or under construction in the U.S. today. Tennessee Eastman will use the process principles to produce acetic anhydride from coal at their Kingsport, TN plant, scheduled to come on-line in Fall, 1983; large indirect liquefaction plants are operated in South Africa to produce primarily motor fuels. The indirect process will not be considered further as a source of industrial boiler fuels.

Direct liquefaction processes fall into one of three categories: carbonization, extraction, and hydrogenation. Very little development work has occurred in the first two categories over the last five years and no commercial plants are under serious consideration. Hydrogenation processes do show some promise of eventually contributing to boiler fuel supplies.

Of the hydrogenation processes, the four which have reached the most advanced state of development are the SRC-I, SRC-II, H-Coal, and Exxon Donor Solvent (EDS) processes. The process descriptions provided in the Synthetic Fuels ITAR are generally accurate with the following exceptions:[24]

- Use of TSL in the SRC-I Process - In an effort to increase the yield of clean premium fuels and the efficiency of hydrogen utilization, a second stage of hydrogen processing has been added to the SRC-I process. In the first stage, raw coal is converted into solvent refined coal (SRC), distillates, and fuel gas. In the second stage, expanded-bed catalytic hydrogenation is used to produce high quality liquids and solids from a portion of the first-stage SRC.[25] For the 6000 tons per day demonstration plant proposed for Newman, KY (see Figure 4.4-1), one-third of the first-stage SRC will be solidified as solid, another third will be feedstock for a delayed coker/calciner to produce anode coke, and the final third will be treated in the second-stage hydrocracker.[26]

- Use of Critical Solvent Deashing in the SRC-I Process - A second major technical change to the SRC-I process is the use of the Kerr-McGee Critical Solvent Deashing (CSD) process for solid-liquid separation in place of filters. This process uses a deashing solvent to extract

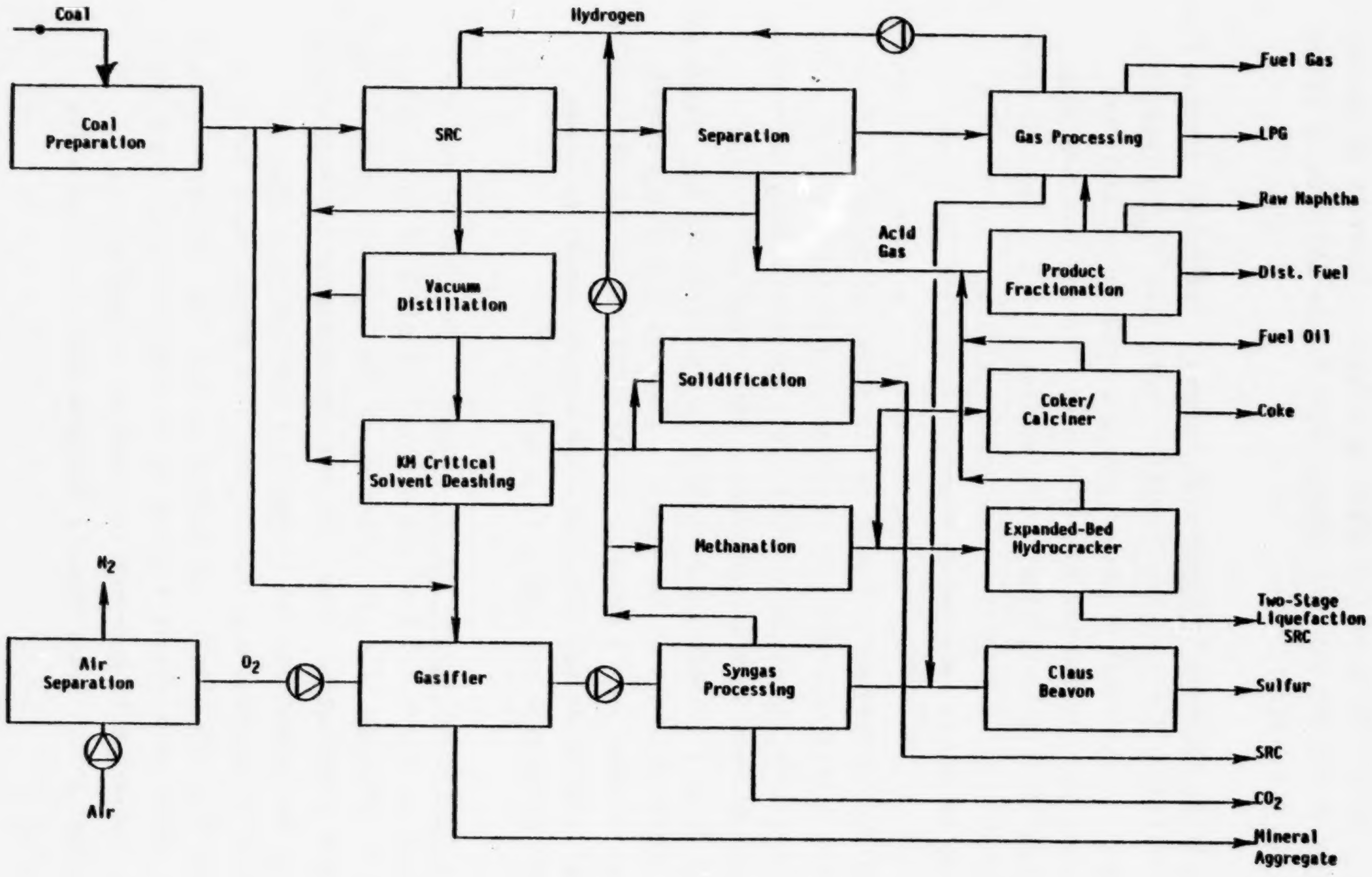


Figure 4.4-1. Flow Digram for SRC-I Demonstration Plant

soluble coal liquids and reject the mineral matter and unconverted coal near the critical point of the deashing solvent. Recovery of approximately 90% of the SRC has been demonstrated by the CSD process at the Wilsonville pilot plant.[27]

- Use of Solvent Deashing in the H-Coal Process - The H-Coal process flow diagram in Figure 2.3-2 of the Synthetic Fuels ITAR is significantly out of date. The H-Coal process can be operated in two different modes: the syncrude and the fuel oil modes. In the syncrude mode, high yields of distillate liquids are achieved. Hydroclones are used to reduce the solids content of the reactor effluent slurry. The low-solids stream is recycled as slurry oil for feed coal; the high-solids stream is fractionated to produce an all-distillate product and a residuum stream which can be fed to a partial oxidation (i.e., gasification) unit to produce hydrogen or used as in-plant fuel. In the fuel-oil mode, a heavier product slate is generated by operating the reactor at less severe conditions. Heavy fuel oil will be recovered using a solvent deashing technique such as the Kerr-McGee CSD process described above or the Lummus anti-solvent deashing process. The latter process uses a promotor liquid which causes precipitation of heavy coal liquids on ash particles. Separation occurs as these particles agglomerate and settle in a settler.[28]

- Use of Partial Oxidation in the EDS Process - The flow diagram for the EDS process in Figure 2.3-2 of the Synthetic Fuels ITAR shows that hydrogen is produced by steam reforming of the light hydrocarbon gases from vacuum distillation. Fuel gas and liquid products are generated by feeding the vacuum bottoms stream to a Flexicoking unit. An alternative arrangement was investigated in a design study for a commercial size EDS plant: the bottoms stream from the vacuum column is split, with about one-half going to the Flexicoking unit and the remainder converted to hydrogen in a partial oxidation (i.e., gasification) unit. Study results indicate that the alternative arrangement leads to a significant improvement in yield and plant thermal efficiency and a slight reduction in capital investment.[29]

- Use of Atmospheric and Vacuum Distillation for the SRC-II Process - Figure 4.5-6 of the March 1982 BID indicates that liquid product from the letdown and flash system of the SRC-II process is directed to a vacuum column for solids removal followed by an atmospheric column for separation of recycle solvent and liquid products. This is no longer an accurate representation of the process as currently configured. The process flow diagram for the proposed SRC-II demonstration plant (see Figure 4.4-2) shows that reactor effluent flows through a series of vapor-liquid separations where it is ultimately separated into process gas, light hydrocarbon liquid, and product slurry. The product slurry is split into two streams, the first being recycled to the process for slurrying with feed coal and the second directed to a vacuum tower. In the vacuum tower, a lighter distillate stream is removed overhead and sent to fractionation; a heavier distillate product is removed as a side stream, and the residue is sent to a gasification unit for hydrogen production. The vacuum tower overhead, together with the light hydrocarbon liquid from vapor-liquid separation, are sent to an atmospheric fractionation tower to produce naphtha and a middle distillate stream. Atmospheric tower bottoms are returned to the vacuum tower.[30]

4.4.2 Factors Affecting Performance

From the standpoint of New Source Performance Standards for industrial boilers, the most important performance criteria for coal liquefaction processes are the reduction of sulfur, nitrogen, and ash contents from parent coals to product liquids and the combustion characteristics of product liquids. In the liquefaction process, sulfur and nitrogen in parent coal react with hydrogen to form hydrogen sulfide (H_2S) and ammonia (NH^3), respectively. Ash in the parent coal is removed via distillation and solids-liquid separation techniques (e.g., hydroclones, filters, ad solvent

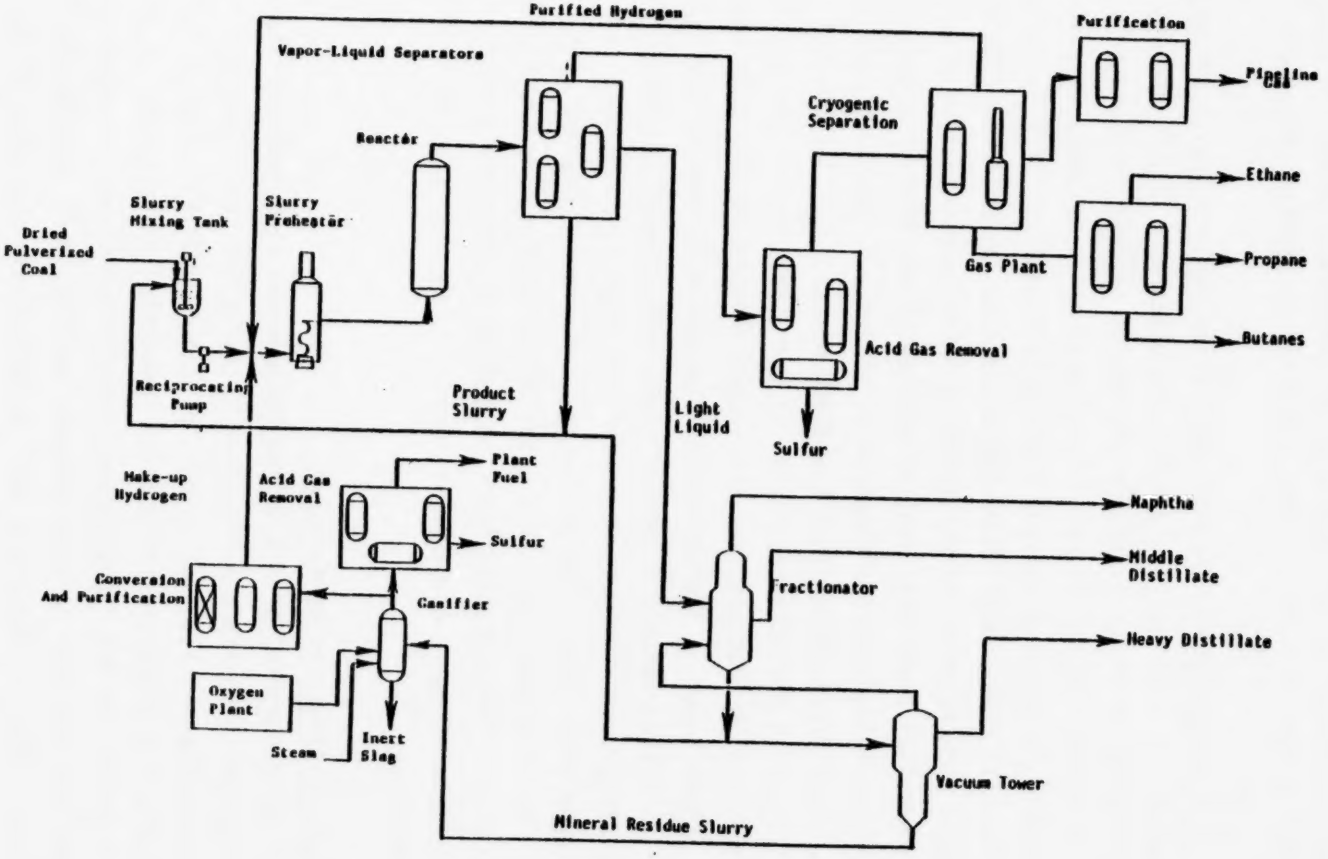


Figure 4.4-2. Flow Diagram for SRC-II Demonstration Plant[30]

deashing processes). The Synfuels ITAR provides a thorough discussion of the impacts of key process parameters on liquefaction product characteristics.[31] The principal impacts have been summarized in Section 4.5.5.2 of the BID.

One other parameter which has been found to be of importance to the combustion properties of SRC is the solids-liquid separation scheme. Combustion Engineering, in a study funded by EPRI, examined the combustion characteristics of SRC produced by pressure filteration deashing (PFD), anti-solvent deashing (ASD), and critical solvent deashing (CSD) under combustion conditions similar to those achievable in boilers originally designed for coal firing. The major conclusions drawn from the study include[32]:

- From an overall combustion efficiency standpoint, both the CSD and PFD SRC are relatively reactive solid fuels comparable in reactivity to subbituminous coal. The ASD SRC is relatively unreactive in comparison.
- Compared to PFD and ASD, CSD SRC has the potential for producing a low carbon (<10%) fly ash under low NO_x, staged combustion conditions if flame temperature can be maintained sufficiently high during both fuel-rich and fuel-lean stages, thereby making the CSD fly ash amenable to collection in electrostatic precipitators.
- The SRC's, due to their relatively high fuel nitrogen contents, have a high NO_x formation potential under conventional firing conditions. However, staging the combustion air can result in lower NO_x emissions without jeopardizing their combustion efficiencies.

4.4.3 Applicability to Industrial Boilers

Commercial coal liquefaction facilities, if built, will produce fuels in much larger quantities than are required by any one industrial boiler. Therefore, the liquefaction plant would be considered an off-site supplier of fuel.

The solid fuel from the SRC-I process cannot be used in conventional stoker boilers but can be used in pulverized coal-fired boilers with minor modifications. Solid SRC cannot be used as speader stoker feed due to its low melting point (approximately 155°C); the SRC would melt on the grate before being combusted and fall into the plenum for removal with the ash.

Satisfactory combustion of solid SRC has been demonstrated for pulverized coal-fired boilers with only minor modifications. Depending on the site, these modifications may include the use of water-cooled burners, addition of moisture prior to pulverization, or minor adjustments to pulverizers. Combustion tests by DOE/PETC, discussed below, have shown that SRC may be fired as a pulverized solid, a molten liquid, or as a slurry with recycle process solvent.

The data presented in Table 2.3-6 of the Synthetic Fuels ITAR for solid SRC and parent coals support the following comparisons:

- SRC ash contents are significantly reduced from parent coal levels to around 0.3 percent;
- SRC heating values are about 25% greater than parent eastern coals and 50% greater than parent western coals;
- The SRC sulfur content for eastern coals can be reduced to 0.7 to 1.0 percent under normal reactor conditions. Even lower sulfur content SRC can be produced by increasing the severity of reactor operating conditions. For western coals, SRC sulfur contents as low as 0.1 percent can be achieved under normal conditions. On a lb $SO_2/10^6$ Btu basis, these sulfur figures correspond to over 80% reduction for eastern coals and almost 90% for western coals.
- SRC fuels have slightly higher nitrogen and hydrogen contents than parent coals and significantly lower oxygen contents.

Coal-derived liquids from the SRC-II, H-Coal, and EDS processes can be substituted for petroleum-based fuels in oil-fired industrial boilers with only minor modifications for coal liquid handling and storage. Studies by Gulf on SRC-II fuel oil showed satisfactory performance with respect to viscosity, flash point, pour point, and stability. However, many elastomers commonly used in fuel handling systems were destroyed by simple swelling tests; viton and nylon 616 being the exceptions.[33]

The coal liquefaction processes cited above produce a variety of fuel oil products with characteristics ranging from those of No. 2 fuel oil to those of No. 6 fuel oil. The data summarized in Table 2.3-5 of the Synthetic Fuels ITAR and Table 4.4-1 support the following general observations:[34,35]

- Coal liquid sulfur contents will range from 0.2 to 0.4 percent under normal conditions compared to 0.04 to 0.5 percent for petroleum products. As with solid SRC, the sulfur (and nitrogen) content of a given coal liquid product can be reduced by adjusting the operating conditions of the reactor and/or hydroprocessing operations;
- The nitrogen content of SRC-II fuel oils is significantly higher (at 0.9 to 1.2 percent) than petroleum products (less than 0.3 percent); nitrogen contents for H-Coal and EDS distillate are comparable to petroleum products.
- Heating values for coal liquids are slightly below those for petroleum products and tend to increase with increasing process severity;
- The oxygen contents of coal liquids (at 1-3 percent) are significantly above those of petroleum products (at 0.01-0.4 percent);
- Coal liquids are more aromatic in nature than petroleum products, which is consistent with their lower hydrogen contents.

4.4.4 Development Status

At this time, no large demonstration-size or commercial-size coal liquefaction plants are operating or under construction. As identified in the Synthetic Fuels ITAR, the SRC-I process has been investigated at the 45 TPD pilot plant in Ft. Lewis, WA and the 6 TPD pilot plant in Wilsonville, AL; the SRC-II process was developed at the Ft. Lewis pilot plant; the EDS process has been under development at a 227 TPD pilot plant in Baytown, TX; and the H-Coal process has been demonstrated at a 546 TPD pilot plant in Catlettsburg, KY.[36] At the present time, operations at all of these pilot plants have been terminated with the exception of the Wilsonville plant.

TABLE 4.4-1 PROPERTIES OF SRC-II FUEL OILS AND COMPARABLE PETROLEUM PRODUCTS[37]

	SRC-II MIDDLE DISTILLATE (350°-550°F)	NO. 2 FUEL OIL	SRC-II HEAVY DISTILLATE	NO. 5 FUEL OIL
ANALYSIS (DRY): % BY WT.				
CARBON	86.0	87.0	89.1	88.3
HYDROGEN	9.1	12.8	7.5	10.7
NITROGEN	0.9	<0.2	1.2	<0.3
SULFUR	<0.2	0.04-0.48	0.37	0.07-1.9
OXYGEN	3.6	<0.09	1.4	<0.4
SATURATES: % BY VOL.	35	>65	-	-
AROMATICS: % BY VOL.	62	<32	-	-
DENSITY	0.974	<0.876	1.072	0.940
VISCOSITY: SUS @ 100°F	36.3	32.6-37.9	231	124-900
FLASH POINT: °F	>160	>130	-	-
POUR POINT: °F	<-45	<+5	<+45	<+80
NICKEL: ppm	<0.1	<0.1	<0.3	46
VANADIUM: ppm	<0.1	<0.1	<0.1	180
SODIUM: ppm	-	<0.5	2-11	2-20

Commercial design studies have been completed for all four processes. Various levels of detailed design have been completed for demonstration plants (nominally 6000 TPD of coal feed) for the SRC-I and SRC-II processes; no firm commitments are in place to construct and operate these plants due to the withdrawal of support by the U.S.DOE and the lack of necessary support from the private sector.

In view of the long lead times associated with the design, construction, and start-up of plants of this size, it seems certain that significant quantities of coal-derived liquid and solid fuels will not be available to industrial boiler operators for the next five years, and probably will not be available for the next ten years.

4.4.5 Reliability

To date, no commercial coal liquefaction plants have been built and only limited combustion tests have been performed on the coal-derived liquids. As a result, information regarding maintenance requirements and the impact these coal-derived fuels would have on an industrial boiler are not available. However, the impacts and maintenance requirements for coal liquids-fired boilers should be similar to those of oil-fired boilers.

4.4.6 Emissions Data

The results of three major combustion tests performed with coal-derived solid and liquid fuels are discussed in this section. These results are primarily concerned with sulfur dioxide, nitrogen oxides, and particulate matter emissions.

Plant Mitchell Tests on SRC-I - An 18-day test burn on solid SRC was conducted in the 22.5 MWe Unit 1 boiler of Georgia Power Company's Plant Mitchell near Albany, Georgia on June 14, 1977. Boiler modifications which were made to accommodate the burning of SRC included:

- Use of specially developed water-cooled dual register burners, and
- Use of ambient primary air, reduced ball spring pressure, and variable speed feeder motors in the pulverizers.

The SRC fuel was produced at the Ft. Lewis pilot plant from approximately 3.9 percent sulfur coal. As fired, the SRC had a heating value of 15,274 BTU/lb, sulfur content of 0.71 percent, nitrogen content of 1.60 percent, and ash content of 0.57 percent. Boiler efficiency while firing SRC was equivalent to that of coal-firing at full load and averaged near 86%. Emissions results for SO_2 and NO_x are summarized in Table 4.4-2. Two ESP's were operated in series after the boiler but the design for the first precipitator was considered to be obsolete. The respective average particulate emissions into the first precipitator, after the first precipitator, and after the second precipitator were 1.0, 0.9, and 0.04 $lb/10^6$ BTU.

The Plant Mitchell tests demonstrated that SRC could be successfully fired in a pulverized coal boiler and meet EPA emission requirements in force in 1977. In addition, the SRC tests demonstrated overall low ash loading and a non-abrasive ash which are expected to mitigate problems with tube cutting and boiler deslagging and generally reduce maintenance on ash handling equipment.

Consolidated Edison Tests on SRC-II Fuel Oil - In September/October, 1978, a combustion demonstration test using SRC-II fuel oil was conducted on a 450,000 lb steam/hr utility boiler located at the 74th Street Generating Station of the Consolidated Edison Company of New York.[38,39] The SRC fuel oil was produced at the Ft. Lewis pilot plant from a variety of parent coals. The heating value, sulfur content, nitrogen content, and ash content of the fuel were 17,081 BTU/lb, 0.22, 1.02, and 0.02 percent, respectively. The objectives of the test were to demonstrate combustion of SRC-II fuel oil, to characterize NO_x emissions, and to investigate the potential to reduce NO_x levels through combustion modifications. Major results of the test program can be summarized as follows:

- No major operational problems were encountered due to combustion of SRC-II fuel oil and performance on SRC-II fuel oil met all applicable emission regulations;

TABLE 4.4-2 EMISSION RESULTS FOR SRC TEST BURN AT PLANT MITCHELL[35]

CONDITIONS	O_2 (%)	SO_2 (ppm)	SO_2 (lb/10^6 BTU)	NO_x (lb/10^6 BTU)
Low Load	11.0	222	1.09	0.43
Medium Load	7.3	255	1.00	0.45
Full Load	5.6	335	0.97	0.40

- Boiler thermal efficiency levels with SRC-II fuel oil were comparable to those with No. 6 fuel oil;
- Nitrogen oxide emissions for SRC-II fuel oil at full load were 0.35 lb/10^6 BTU at baseline conditions and 0.23 lb/10^6 BTU at low NO_x (staged combustion) conditions. NO_x emissions for SRC-II fuel oil were nominally 70% greater than those for No. 6 fuel oil at both conditions. This result was expected in view of SRC-II fuel oil's higher nitrogen content.
- Use of staged combustion reduced NO_x emissions on the order of 35% for both SRC-II and No. 6 fuel oils.
- Particulate emissions for SRC-II fuel oil were below 0.03 lb/10^6 Btu under all test conditions and typically 40-60 percent lower than equivalent emissions for No. 6 fuel oil.

It should be noted that the test boiler in this program was ideally suited to take maximum advantage of the staging concept (i.e., a well-mixed flame in the fuel rich zone, and adequate space for soot burn-out in the fuel lean zone).[40] The NO_x emissions level which can be anticipated with other types of boilers with more intense flames is not certain.

DOE/PETC Tests on SRC - Tests were conducted with solid SRC using a 3450 lb steam/hr firetube boiler, designed to burn No. 6 fuel oil, at the U.S. Department of Energy's Pittsburgh Energy Technology Center (PETC).[41] The tests were designed to demonstrate the feasibility of using this fuel in more compact oil and gas-fired units with higher heat release rates than the coal-fired utility boiler of the Plant Mitchell test. The fuel was produced at the SRC pilot plant in Wilsonville, AL from high-sulfur Kentucky coal. The solid SRC had a heating value of 15,927 Btu/lb, sulfur content of 0.8 percent, nitrogen content of 2.0 percent, and ash content of 0.3 percent. The SRC was fed to the boiler in three different physical forms: a slurry of 70 percent SRC-I process solvent and 30 percent pulverized SRC; a molten liquid at approximately 600°F; and a solid, pulverized to 90 percent minus 325 mesh. The major results of the program are summarized below:

- Carbon conversion and boiler efficiencies for slurry and molten forms were equivalent to those for No. 6 fuel oil (at 99.7 percent and 82 percent, respectively).
- For pulverized SRC, boiler efficiency was the same but carbon conversion efficiency was slightly reduced (98.6 to 99.6 percent); pulverized SRC was burned at 50 percent load due to burner limitations.
- Emissions results are summarized in Table 4.4-3. The data suggest that SO_2, NO_x, and particulate emissions are proportional to the sulfur, nitrogen, and ash contents of the respective fuels.
- Results indicate that SRC, including the solid form, can be burned in larger oil-designed boilers of watertube design without significant derating.

TABLE 4.4-3 EMISSION RESULTS FOR DOE/PETC TESTS ON SRC [39]

EMISSIONS ($lb/10^6$ BTU)	NO. 6[a] FUEL OIL	SRC/SOLVENT[a] SLURRY	MOLTEN[a] SRC	PULVERIZED[b] SRC
SO_2	0.628-0.671	0.537-0.693	0.953-1.085	1.130-1.194
NO_x	0.223-0.265	0.668-0.850	0.669-0.772	0.770-1.134
Particulate Matter	0.139	0.122-0.214	0.184-0.849	0.13-0.70

[a] Full Load
[b] Half Load

4.5 REFERENCES

1. Buder, M.K., et al. (Bechtel National, Inc.), Impact of Coal Cleaning on the Cost of New Coal-fired Power Generation. EPRI CS-1622. March 1981. p. 4-9. 129.

2. Buroff, J., et al. (Versar, Inc) Technology Assessment Report for Industrial Boiler Applications: Coal Cleaning and Low Sulfur Coal. Publication No. EPA-600/7-79-178c. December 1979. p. 124.

3. Reference 1, p. 127.

4. Jung, A., et al., (Versar, Inc.) Determination of the Attenuation of Sulfur Variability by Coal Preparation. Draft Report. EPA Contract No. 68-02-2199. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory. Research Triangle Park, N. C. March 1981.

5. Bituminous Coal and Lignite Production and Mine Operations - 1978, U.S. DOE/Energy Information Administration, Energy Data Report, Publicatin No. DOE/EIA-0118(78), June 16, 1980. p. 55.

6. 1982 Keystone Coal Industry Manual. New York, McGraw-Hill Inc., 1982.

7. Cavallaro, J. A., et al. (U. S. Bureau of Mines). Sulfur Reduction Potential of U. S. Coals: A Revised Report of Investigations, BOM RIV 8118, Publication No. EPA/600/2-76-091. April 1976. pp. 296, 312, 314, 321, 322.

8. Letter from J. A. Maddox (Radian) to Stan Curtis (Caterpillar), May 23, 1984.

9. Proceedings of the Fifth International Symposium on Coal Slurry Combustion and Technology. Sponsored by the U. S. DOE (Pittsburgh Energy Technology Center). Tampa, Fl. April 25-27, 1983. p. 314, 502-521, 580-587.

10. Reference 9, p. 502.

11. Proceedings of the Third International Symposium on Coal-Oil Mixture Combustion. Sponsored by the U.S. DOE (Pittsburgh Energy Technology Center). Orlando, Fl. April 1-3, 1981. p. 114, 171-183.

12. Reference 11, pp. 171-183.

13. Proceedings of the Ninth Annual International Conference on Coal Gasification, Liquefaction and Conversion to Electricity. Sponsored by the University of Pittsburgh and the U. S. DOE (Pittsburgh Energy Technology Center). Pittsburg, PA. August 3-5, 1982. p. 210.

14. Reference 9, p. 580-587.

15. Foo, O. K., et al. An Assessment of Package Boilers for Industrial Coal-Liquid Mixture Applications. (Presented at the Fourth International Symposium on Coal Slurry Combustion and Technology. Orlando, Florida.) May 10-12, 1982.

16. Hawkins, G. T. (Coal Liquid, Inc.). Industrial Utilization of Coal-Oil Mixtures, (Presented at Coal Technology '81 Conference. Houston, Texas. November 17-19, 1981.) pp. 215-224.

17. Synfuels, March 11, 1983, p. 4.

18. Synfuels, March 18, 1983, p. 4.

19. Reference 9, pp. 502-521.

20. Chemical Engineering, April 18, 1983, p. 27, 29.

21. Chemical Engineering, June 27, 1983, p. 15.

22. Pan, Y. S. et al. Coal-Methanol Mixture Combustion Tests with Coals of Different Ranks. (Presented at the Fifth International Symposium on Coal Slurry Combustion and Technology. Tampa, FL. April 25-27, 1983.)

23. Thomas, W. C. (Radian Corporation.) Technology Assessment Report for Industrial Boiler Applications: Synthetic Fuels. (Prepared for U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina. Publication No. EPA-600/7-79-178d. November 1979. pp. 2-38 - 2-50, 2-54.

24. Reference 23, pp. 2-38-2-50.

25. Smith, M. R., D. A. Hubbard, and C. C. Yang (Kellogg-Rust Synfuels, Inc.). Logic Technology and Effect of Coal Liquefaction Conditions on Final Up-Graded Product State. Proceedings of the Ninth Annual Conference on Coal Gasification, Liquefaction and Conversion to Energy. Pittsburgh, PA. August 3-5, 1982. p. 440, 438.

26. Tao, J. C. and J. P. Jones (International Coal Refining Co.). SRC-I Technology and Its Economics. Energy Progress. 3(1):2. March 1983.

27. Reference 25, p. 438.

28. Eccles, R. M. and G. R. DeVaux (Hydrocarbon Research Inc.). Current Status of H-Coal Commercialization. Chemical Engineering Progress. May 1981. pp. 80-85.

29. Epperly, W. R. and D. T. Wade (Exxon Research and Engineering Co.). Donor Solvent Coal Liquefaction. Chemical Engineering Progress. 77(5):73-79. May 1981.

30. Freel, J., D. M. Jackson and B. K. Schmid (SRC International, Inc.). The SRC-II Demonstration Project. Chemical Engineering Progress. 77(5):86-91. May 1981.

31. Reference 23, p. 2-54.

32. Goetz, G. J., T. C. Lao, A. K. Mehta, and N. Y. Nsakala (Combustion Engineering, Inc.). Effect of Liquefaction Processing Conditions on Combustion Characteristics of Solvent-Refined Coal. Interim Report. (Prepared for Electric Power Research Institute. Palo Alto, California.) Publication Number AP-2328. March 1982. pp. S-1 - S-7.

33. Freel, J. and D. M. Jackson (SRC International, Inc.) SRC-II Product Applications-Recent Developments. Proceedings of the Eight Annual International Conference on Coal Gasification, Liquefaction and Conversion to Electricity. Pittsburgh, PA. August 4-6, 1981. pp. 231-233, 241, 242-243, 232.

34. Reference 23, p. 2-54.

35. Reference 33, p. 241.

36. Reference 33, p. 2-42 - 2-43.

37. McRanie, R. D. (Southern Company Services, Inc.). Full-Scale Utility Boiler Test With Solvent Refined Coal (SRC). Interim Report. Work Performed Under U.S. Department of Energy Contract No. EX-76-C-01-2222. April 1978. pp. 1-15.

38. Piper, B. F., S. Hersh, and W. Nazimowitz (KVB Incorporated). Combustion Demonstration of SRC-II Fuel Oil in a Tangentially Fired Boiler. Final Report. (Prepared for Electric Power Research Institute. Palo Alto, California. May 1979.) pp. 7-1 - 7-22.

39. Hersh, S., et. al. (KVB Incorporated). Emissions Characterization of SRC-II Fuel Oil Fired in a Utility Boiler. Proceedings of the Governor's Conference on Expanding Use of Coal in New York State: Problems and Issues. 1981. pp. 323-329.

40. Reference 33, p. 232.

41. Pan, Y. S., et. al., (U.S. Department of Energy). Final Test Report on the Combustion of Solvent Refined Coal in a 100-HP Firetube Boiler. (Prepared by Pittsburgh Energy Technology Center, Pittsburgh, PA.) Publication No. DOE/PETC/TR-82/5 (DE 82007670). pp. 17-22.